Chapter 2
Biofuels: Production Technologies, Global Profile, and Market Potentials

Abstract In spite of the benefits associated with the production and consumption of biofuels, there are some crucial debatable issues like high cost, food insecurity, etc., that put them to the negative side. However, biofuels still hold impressive market potentials in the world today though most of their production technologies are sophisticated and costly. Liquid biofuels like bioethanol and biodiesel are commonly produced from feedstocks like corn, rapeseed, soybean, etc., but there are other potential feedstocks, which are more sustainable like palm oil. This chapter discusses the major sources of biofuel feedstocks, types of biofuels, their production technologies, and global market potentials.

Keywords Biofuels market · Palm biofuels · Liquid biofuels · Solid biofuels · Gaseous biofuels · Oil palm biomass · Palm oil · Biofuel production · Transesterification · Pyrolysis · Anaerobic digestion

2.1 Introduction

Presently, fossil fuels such as coal, crude oil, etc., which have been the main sources of energy in the world since the late 1930s, form about 82–86 % of the world's total energy (IEA 2010; Dorian et al. 2006). In 2011, Biofuels contributed about 2 % (about 55 mtoe)[1] of the world's total transportation fuels (EIA 2011) with their associated feestocks cultivation claiming around 2 % of the world's total arable land (WWI 2006). Over the past decade, the production of biofuels has gained much attention mainly due to the negative impacts of the conventional fuels

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[1] A million ton of oil equivalent (mtoe) is approximately equal to 41.87 GJ. Thus, in 2011, biofuels contributed about 2302.85 GJ energy to the world's transportation sector and this is expected to increase to about 750 mtoe in 2050 (EIA 2011).

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(especially fossil fuels) on the environment. The most threatening aspect involved with the use of fossil fuels has been their near exhaustion and fluctuations in prices globally. Because biofuels are renewable, they present relatively cheap (i.e., when fossil fuels nearly get exhausted and their prices go high) and secured energy supply in the long term. Sustainable development worldwide cannot be realized with the continuous production and consumption of fossil-based fuels thus the pressing need to promoting sustainable agriculture leading to the sustainable production and consumption of biofuels worldwide.

Biofuel production worldwide has been increasing tremendously in capacity since the year 2000 with major contributing regions and countries being the USA, Brazil, the European Union (EU), China, Malaysia, and India (IEA 2010). Asian countries are forecast to triple their production in the future utilizing feedstocks such as *Jatropha curcas L.*, oil palm, etc., that thrive well in tropical climates. Although the cultivation of certain feedstocks and the applications of inefficient technologies for biofuels production may have detrimental effects on the land, water, and biodiversity, one crucial environmental benefit of their consumption has been their insignificant contribution to greenhouse gas (GHG) emissions during combustion. However, the energy and GHG balances need to be effectively intensified in order to generate clean energy throughout their life cycles. This chapter discusses the potential impacts of biofuel types on global market as well as the global production and consumption status. Of late almost all the continents of the world especially North America, the USA, the EU, Asia, and some parts of Africa have prioritized biofuels as transportation fuels and are working hard to offset most of the major drawbacks associated with their production. Though some of these countries (especially the developing ones) have not yet implemented renewable energy regulations, which mandate subsidies and incentives for biofuel producers, the interest in biofuel production is still growing from strength to strength.

2.2 Types of Biofuels and Their Feedstocks: An Overview

Biofuels are either liquid, solid, or gaseous fuels that are derived from the conversion of biomass (organic matter). The energy from biomass is derived from the process of photosynthesis, which utilizes the sun's energy to emit electrons from water molecules. Although fossil fuels have their origin from organic matter, they are not considered biofuels because it takes millions of years (at least 20 million years) for the earth to transform dead organic material into these fossil fuels (which are nonrenewable). Biofuels, on the other hand, are renewable fuels whose feedstocks do not take very long time to grow or ripe for harvest as compared to fossil fuels. However, biofuels are not considered carbon neutral because fossil fuels are used heavily during the cultivation of their feedstocks (e.g., the use of fossil fuel like diesel by irrigation equipment, tractors, etc.) and conversion processes

Table 2.1 Characterization of feedstocks for biofuel production

Feedstock type	Classification	Sources
1. First generation	1. Food (energy) crops	1. Rape seed, soybeans, sunflower seeds, canola, camelina, palm fruits, babassu kernel, coconut kernel, cotton seeds, wheat, barley, sugarcane, cassava, corn/maize
	2. Animal fats	2. Lard, animal intestines, animal parts
2. Second generation	1. Agricultural residues	1. Lignocellulosic materials such as straw, grass, leaves, prunings (such as palm fronds), miscanthus, willow, corn stover, rice husks, palm empty fruit bunches, poplars, eucalyptus, reed canary grass, short-rotation, broadleaved coppice, etc.
	2. Forest residues	2. Lignocellulosic materials like wood chippings, branches, foliage, roots, etc.
	3. Animal and oil wastes	3. Animal manure, tallow, chicken fat, fish oils, waste cooking oil
	4. Nonfood (energy) crops	4. Jatropha seeds, soap nut seeds, mahua seeds (*Madhuca indica),* indian beech/pongame seeds *(Pongamia pinnata),* karanj seeds, castor beans, Hemp, monkey cola (*Carapa procera*), etc.
	5. Biowastes streams	5. Municipal solid wastes (e.g., kitchen/household wastes, construction wood wastes, packaging wastes, etc.), sewage sludge, industrial liquid wastes such as process effluents
3. Third generation *(green, brown and red algae)*	1. Microalgae	1. Botryococcus, Chlamydomonas, chlorella, spirulina, etc.
	2. Macroalgae (macrophytes or seaweeds)	2. Cladophora, Spirogyra, Hydrodictyon, *Batracho spermum*, Halimeda, Maiden's Hair, Caulerpa, etc.

into biofuels.[2] Moreover, as the biofuel industry experiences impressive growth year by year, the production of raw materials also keep creating biodiversity loss as they require land, water, and other resources, which are used for food crop cultivation. Though these and other drawbacks of biofuels exist, they are still environmentally friendly compared to fossil fuels. Biofuels are classified according to the source of feedstock used and the type of fuel produced. Table 2.1 summarizes the common kinds of biomass or feedstocks used for biofuel production.

Biofuels may be in the form of *liquid* such as bioethanol, biodiesel, and pyrolysed oil; *solid* such as firewood, wood pellets, palm kernel shells, sugarcane bagasse, etc; or *gas* such as biogas, syngas, biohydrogen, etc. Solid fuels are not intensely processed (often called *primary biofuels*) and can be directly combusted to release energy for cooking, heating, and electricity generation. Biofuels produced from processed feedstocks (often called *secondary biofuels*) like bioethanol, biodiesel, biogas, charcoal, hydrogen, etc., are mostly used for transportation purposes and high temperature industrial applications. The biomass used as fuel may also be sourced from by-products, co-products, fibers, lignocellulosic materials, which are generated during the production of food products. For instance, black liquor, palm wastes such as oil palm fronds, palm kernel shells, coffee husks, etc., are fuel sources, which are directly combusted to produce energy (in the form of heat and electricity) in many countries of the world.

Depending on the source of feedstock for production, biofuels are classified as first-, second-, and third-generation biofuels (Larson 2008). *First-generation biofuels* (FGB), also called ‘conventional’ biofuels are the type of biofuels,[3] which are produced from first-generation feedstocks (FGF) specifically food crops (e.g., sugar, starch, vegetable oil, animal fats, etc.) and have successfully established firm foundations for second- and third-generation biofuels as their technologies and developments are quite simple. The potential impacts of FGB are immensely linked to the efficient cultivation of the feedstocks as they require land, water, fertilizer, and other materials, which may eventually create environmental hazards and above all food insecurity. These and other drawbacks have been current debatable issues concerning the use of FGF for biofuels production in the world.

Biodiesel production from palm oil, for instance, could record significant GHG savings if the cultivation of the oil palm is done on already used land, which needs no intensive bush clearing, and most importantly, fertilizer and other resource use are minimized. Moreover, since the value of biofuels in connection with carbon abatement cost has direct impacts on the GHG emissions and biofuel production costs, there is the need to efficiently manage the various processes involved in biofuels production. This would eventually reduce the abatement cost of using

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[2] Unless all the input resources (both materials and energy) are sourced from renewable sources, biofuels would not be considered carbon neutral though their contributions to GHG emission may be negligible.

[3] FGB include biodiesel from rapeseed oil, bioethanol from wheat, biogas from corn etc.

FGB, which is often as high as US$ 200–800/ton CO_2 avoided[4] (CBO 2009). Though FGB are found to exhibit a net benefit in terms of greenhouse gas (GHG) emissions reduction and energy balance, they also have several drawbacks which are outlined in Table 2.2.

Second-generation biofuels (SGB) are biofuels produced from nonfood energy crops, agricultural and forest residues. Though currently, only a few SGB production plants are commercialized (because of technologically unproven efficient conversion of SGF into biofuels), they are expected to overtake FGB in terms of energy balance, GHG emissions reduction, competition of land for food and above all high biofuel yield which are significantly higher than those for most FGB. Lignocellulosic materials that are mostly used as feedstocks for bioalcohol production are found in abundance (with annual production of 10–50 billion tons in dry weight) all over the world (Galbe and Zacchi 2002). However, only about 10 % are sustainably utilized for value-added bioproducts with the remaining being burnt and dumped at unauthorized places creating environmental burdens. Meanwhile, these materials often regarded as wastes could generate bioenergy amounting to about 100 EJ per year (Galbe and Zacchi 2002).

Biofuels from lignocellulosic materials are more advantageous to some other nonfood energy crops such as *Jatropha curcas L.* because they need no land for major cultivation, which may require certain practices that could contribute to GHG emissions. Again, almost all the lignocellulosic materials available now are considered wastes thus a sustainable waste management option would turn them into ‘wealth’ (biofuels). In the short term, supporting FGB production with government subsidies as well as mandatory consumption policies that are stringently implemented may not allow the tremendous growth of SGB dominating the world.

Third-generation biofuels (TGB) are also known as algae fuels whose feedstock may either be from algae (macroalgae or microalgae) or other aquatic biomass. TGB are presently developed with much interest due to the high yields of oil generated from the feedstocks as well as the capture of carbon dioxide from the atmosphere during the feedstock cultivation (which do not need much arable land for growth). Biofuels from algae presently accounts for less than 1 % of the global total biofuel production capacity though there are many other advantages associated with their productions and use as compared to FGB and SGB.

Fourth-generation biofuels are biofuels that are produced from genetically modified or engineered energy crops and organisms that are able to extract CO_2 from the atmosphere more than what their fuels release on combustion (Lü et al. 2011). Feedstocks for the production of fourth-generation biofuels are modified in such ways that breaking them down (using functionally engineered enzymes) into biofuels are much easier due to their loose cell wall. Research and developments are underway with these types of biofuels to contribute to sustainable biofuels production.

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[4] The use of biofuels to cut down GHG emissions attracts about US$ 754, US$ 275 and US$ 306/ton of CO_2 for corn ethanol, cellulosic ethanol and biodiesel respectively. Again, a taxpayer in USA who used a gallon of corn ethanol, cellulosic ethanol and biodiesel would obtain a credit of US$ 1.78, US$ 3.00 and US$ 2.55 respectively as a way of substituting fossil fuels (CBO 2009).

Table 2.2 Advantages and disadvantages of biofuel types

Benefits	Biofuel type	Drawbacks
1. First generation	1. Net benefit in terms of GHG emissions reduction and energy balance	1. Competition with food crops and water resulting stunted economic growth
	2. Can save up to 50–60 % carbon emissions compared to fossil fuels	2. Higher total production costs (excluding subsidies, etc.) hence expensive to adopt
	3. Production technologies are simple, efficient, and inexpensive compared to the other biofuel types by feedstock source	3. Destruction of biodiversity as forests and lands are cleared to grow the crops
	4. Increased biomass yield per hectare of cultivated land	4. Compete with scarce water resources for irrigation in certain areas of the world
		5. Contribute much to nitrous oxide emissions and have limited GHG reduction potentials
		6. Are not energy efficient during their production processes
		7. Displacement of small scale farmers
2. Second generation	1. Can save up to 80 % carbon emissions compared to fossil fuels	1. High production cost
	2. Positive energy balance	2. Logistics and supply chain challenges e.g., difficulty in feedstock harvesting, storage, transportation, etc.
	3. Readily available and access to sustainable feedstocks which are mostly regarded as wastes	
3. Third generation	1. Noncompetitive with agriculture and water resources	1. Energy intensive and economically unsustainable technology[a]
	2. High oil yield per hectare (more than 100 times) compared to first and second-generation biofuels	2. Due to the presence of polyunsaturated fats, algae biofuels (especially biodiesel) are unstable and most often give rise to poor engine performance
	3. Possible production of different kinds of biofuels (e.g., biodiesel and bioethanol)	
	4. Suitable for use in cold weather due to the presence of high levels of polyunsaturated fats	
	5. Reduction in carbon emissions during feedstock cultivation	

[a] With the current technology for algae biofuels production, their cost ineffectiveness compared to FGB and SGB is a major challenge. An estimated production cost for algae biofuels is more than US$ 8 per gallon compared to US$ 4–5/gal FGB and SGB production. (Davis et al. 2001)

There are basically two main process technologies for producing biofuels, namely, biochemical and thermochemical conversion technologies. Thermochemical conversion processes such as combustion, pyrolysis, gasification, torrefaction, co-firing, combined heat and power (CHP) processes, etc., use heat (and sometimes catalysts) to convert the dried biomass into biofuels (Pramanik 2003). These processes are distinguished by their process conditions such as the use of oxygen and the intensity of heat used. Thermochemical processes such as hydro processing, hydrothermal upgrading are also suitable for wet biomass. Biochemical processes, on the other hand, use enzymes to break down the biomass into biofuels. Such processes include anaerobic digestion, fermentation, composting, transesterification, etc. Each of the technologies is elaborated in the subsequent sections.

2.3 Liquid Biofuels for Transportation Purposes, Heat and Power Generation

Liquid biofuels have been one of the most consumed type of biofuels in the world today. Because they can easily blend or totally substitute petroleum diesel (PD) and gasoline (petrol) as transportation fuels without major modifications to engines and fueling systems, they have attracted much attention and investments. Apart from serving as transportation fuels, they are commonly used in heating and electricity production in most parts of the world. Though many kinds of bio-oils are in use, the commonly used types of liquid biofuels are the first-generation ones mostly biodiesel and bioethanol which represent about 15 and 85 % of the current world's production, respectively (OECD-FAO 2011).

2.3.1 Biodiesel

Biodiesel is a dark or golden brown liquid (depending on the type of feedstock) biofuel, which consists of long chain mono-alkyl esters (depending on the type of alcohol used for its synthesis) of fatty acids produced from biomass-based oil or animal fats that can be blended with PD or used alone. Biodiesel is not only produced from the chemical reaction of lipids with alcohols in the presence of catalysts but also as a product from many other thermochemical processes like pyrolysis. Unlike raw vegetable oil, biodiesel can be used in fuel diesel engines in pure form (i.e., 100 % biodiesel, B100) or when blended with PD in slightly modified diesel engines. Biodiesel blends currently used worldwide include B5 (5 % biodiesel, 95 % PD), B10 (10 % biodiesel, 90 % PD), B20 (20 % biodiesel, 80 % PD), B80 (80 % biodiesel, 20 % PD). B100 and other high-level biodiesel blends (from B25 to B95) are not commonly used compared to B5 and B20 because they are expensive, often require special engine modification and are not commonly covered by subsidies and other policy regulatory incentives. Moreover, high-level blends have lower energy content per liter of biodiesel and can also increase the nitrogen oxides emissions, cause microbial contamination in tanks and often gel in cold temperatures (Levine et al. 2010). American Society for Testing and Materials (ASTM) International specifications (ASTM D975) allows biodiesel blends with PD in concentrations up to 5 % (B5), which is approved for efficient operation in compression ignition engines designed for PD use.

B100 is found to eliminate almost 90 % of air toxins whilst B20 also reduces the air toxins by about 20–40 % (Joshi and Pegg 2007; Marland 2010). Also, the emissions like NOx and SO_2 can also be reduced by almost 20 % when biodiesel blends are used (Joshi and Pegg 2007; Crutzen et al. 2008). B100 and B20 are also found to reduce CO_2 emissions by more than 75 and 15 %, respectively compared to PD (Balat 2005; Radich 2004).

Comparing biodiesel to PD, biodiesel possesses better lubricating properties, higher flash point (>200 °C compared to that of PD (52–96 °C) and gasoline (−65 °C)), higher density (~0.88 g/cm^3 compared to PD at ~0.85 g/cm^3) and higher cetane rating (Yoon et al. 2008; Moser 2009). Biodiesel is immiscible with water and has high boiling point (330–357 °C) and low vapor pressure (<1 mmHg) compared to PD (~8 mmHg). The calorific value of biodiesel (36.76–39.34 MJ/kg) is almost 11 % lower than that of PD (45.46 MJ/kg). These encouraging characteristics of biodiesel make them more suitable for use in diesel engines just like PD (Adebayo et al. 2011) without major modifications.

First-generation biodiesel is basically produced from FGF such as rapeseeds, palm fruits, soybeans, etc. There are several debatable issues about first-generation biodiesel because over 95 % of the current biodiesel in use are produced from edible oils that would continue to create food insecurity in the world if alternatives are not sought. However, the present global production capacity of first-generation biodiesel is not sufficient to replace liquid fossil fuels due to scarcity of land for the cultivation of FGF for biodiesel production. The small percentage of crop land used for FGF cultivation has resulted in global imbalance to food supply and demand market as well as negative environmental impacts (Butler 2006). For instance, in the USA, about 11 million tons and 5.3 million tons of vegetable oils and animal fats are produced annually for many purposes including biodiesel production respectively (EIA 2011). On the other hand, the total PD for transportation as well as crude oil for heating purposes in the USA is estimated at 160 million tons (EIA 2011), which is far higher than the biodiesel which could be produced from soybean oil when the entire arable land area is used. This data show a vast gap between PD and biodiesel produced from FGF thus the need for a more secured alternative feedstock for biodiesel production. Second-generation biodiesel are similar to the first-generation biodiesel in characteristics but produced from nonedible crops such as *Jatropha curcas L.*, karanj, *Capara procera*, etc. unlike edible crops that are used for first-generation biodiesel.

2.3.1.1 Biodiesel Production Technologies

The sustainability of biodiesel production depends on so many factors which include:

- Feedstock sources (e.g., edible crops, wastes oil, pyrolysis oil from biomass, etc.).
- Feedstock type based on the amount of free fatty acids (FFA) in the feedstock (e.g., animal fat, vegetable oil (either refined or unrefined, etc.)).
- Feedstock pretreatment method (e.g., solvent extraction, mechanical extraction, hydrotreating, etc.).
- Type of catalysis employed during the production processes (e.g., base or acid catalysis).
- Type and source of alcohol and other raw materials used (e.g., bioalcohol, conventional alcohol, hydrogen, etc.
- Source of energy used (e.g., fossil fuel, renewable energy, etc.).

Generally, all the above-mentioned factors may affect the cost of biodiesel produced. For instance, high free fatty acid (FFA) feedstocks such as animal fat, waste cooking oil,[5] etc. may result in high processing cost though the feedstock themselves may be cheap (see Chap. 6 for economic sustainability analysis of palm biofuels). About 75–90% of the cost of biodiesel is mostly assigned to the type and amount of resource inputs into its production (Reaney 1997). And therefore the need for better choice of input resources.

There are four main methods of producing biodiesel namely:

- Use of pure or blended vegetable oils directly in diesel engines.
- Catalytic hydrogenation and thermal cracking (pyrolysis) of oils and fats.
- Microemulsion.
- Transesterification reaction.

The direct use of raw or straight vegetable oil (SVO) like peanut oil as fuel in diesel engines have been demonstrated by Rudolf Diesel in 1893 and successfully been applied since then. However, due to some characteristics of these vegetable oils (such as high viscosity which is about 15 % that of PD), the diesel engines may develop problems with time. Again, other disadvantages of using SVO are associated their high cloud points, high surface tension, low cetane number, high flash point, presence of impurities (like phosphatides), susceptibility to the fomation of sludge and coke deposits on combustion (Haas 2005). Solutions to these problems may include (1) refining of SVO to remove gums before use as fuels in engines, (2) preheating of SVO to reduce the viscosity before injection, (3) adjusting injection timing and using quality models of compression engines to avoid engine knocking, which may improve its performance than when used in its pure form.

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[5] FFA levels in animal fats, wastes cooking oil, crude vegetable oil and refined vegetable oil are 10–30, 4–40, 5–65 and 0.01–0.5 % respectively (Marchetti et al. 2008; Liu et al. 2007).

However, blending SVO with PD may also improve the fuel's characteristics significantly but in the long term, engine modifications (which is quite expensive) may be required. A couple of researches have reported the good performances of modified (for long-term use) and unmodified (for short-term use) diesel engines that have been ran on pure SVO such as sunflower oil (Rosca and Zugravel 1997; Cigizoglu and Ozaklam 1997; Schlick et al. 1988), rapeseed oil (Bialkowski et al. 2005), palm oil (Sapvan et al. 1996; Prasad 2010), cotton seed oil (Martin and Prithviraj 2011), coconut oil (Machacon et al. 2001), deccan hemp oil (Hebbal et al. 2006), soya bean oil (Schlick et al. 1988; Niehaus et al. 1985), linseed oil, castor oil, mahua oil, and neem oil (Prasad 2010), etc. Also, the use of blended SVO/PD in diesel engines have been demonstrated by several other researches (Wang et al. 2006; Tadashi 1984; Vellguth 1983; Barsic and Humke 1981). Martin and Prithviraj (2011) have reported a remarkable performance of diesel engine with cotton seed oil when preheated to 70 °C and blended with PD at 60 %. However, Murayama (1984) had previously suggested an increasingly high preheating temperature of 200 °C for improved engine performance. In the UK, the EU, and the USA, rapeseed oil, canola oil, and sunflower oil are blended with PD and used in diesel engines for various purposes. Generally, SVO used in diesel engines present acceptable engine performance and emissions for the short term but operational and durability problems may be encountered in the long-term use.

Simultaneous hydrogenation (also called hydrogenolysis, hydrocracking or hydrotreatment) and catalytic cracking of vegetable oils has recently emerged as one of the efficient methods of producing biodiesel, which was developed by the Saskatchewan Research Council under the sponsorship of the Canada Center for Mineral and Energy Technology (CANMET). A feasibility study on this process has been done using 'tall oil' which is a viscous yellow–black odouriferous liquid generated as residue from the production of chemicals (e.g., during the Kraft process of wood pulping from coniferous trees) as a feedstock to produce biodiesel called "SuperCetane". Tall oil may contain 30–50 % FFA, 40–50 % resin acids and 10–30 % unsaponifiables (Cvengroš et al. 1985). Due to high FFA content of tall oil, they are mostly refined before the hydrogenation process into biodiesel. Apart from CANMET, Coll et al. (2001) have reported the successful transformation of tall oil into biodiesel through the hydrotreatment method.

Hydrogenation of fats and oils is normally carried out in a reactor (operating at 300–500 °C) equipped with stirrer, heating jacket and reflux tunnel (Lappas et al. 2009). Hydrogen gas is injected into the fats and oils at high pressure which then passes through pre-heaters into the catalytic reactor. The product (comprising a straight chain paraffinic hydrocarbons that are free of aromatics, oxygen and sulfur, and have high cetane numbers) is collected, dehydrated, and distilled at atmospheric conditions. Hydrogenation helps prolong the shelf life of the fuel. The deoxygenated liquid fuel produced after hydrocracking of the biomass are reported to be more stable than biodiesel produced from transesterification process, and also, they contain oxygen and double bonds thus suitable for use in cold areas. This

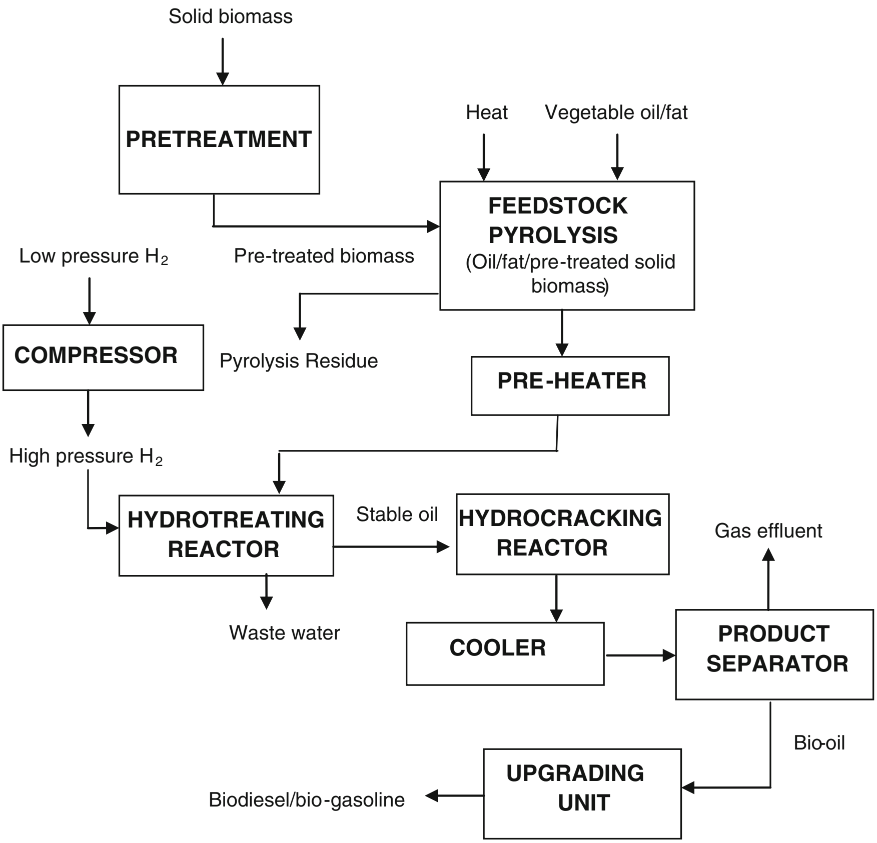

Fig. 2.1 Simplified flow diagram for simultaneous hydrogenation and thermal/catalytic cracking of biomass into bio-oil

method of producing biodiesel and biogasoline has been demonstrated by Nasikin et al. (2009) using palm oil as the feedstock. Figure 2.1 summarizes the production of biodiesel or biogasoline from solid biomass and vegetable oil/animal fat using simultaneous hydrogenation and catalytic/thermal cracking process.

Pyrolysis or thermal/catalytic cracking can also occur independently with hydrogenation of the oils and fats and in this case, no hydrogen is involved. Pyrolysis oils have also been found to possess similar characteristics of PD and can be used in diesel engines though they are not considered complete biodiesel. Pyrolysis oil is highly viscous and basically comprises aliphatic and aromatic oxygenates such as acids, aldehydes, ketones, etc., as well as particulate matter. It has a relatively low energy density of about 19 MJ/kg compared to that of PD (30 MJ/kg) hence may need additional pretreatments before being used as fuels in diesel engines (Solantausta et al. 1994). Thermal/catalytic cracking or pyrolysis is the process of decomposing large molecules into smaller chain compounds by heating at high temperatures (400–550 °C) and atmospheric pressure (Kersten et al. 2007; Solantuasta 2006) anaerobically with or without catalysts.[6]

Zeolite has been reported to possess excellent characteristics as a catalyst for pyrolysis of vegetable oils and fats because of their higher selectivity, thermal stability, ease of separating from the products and the possible regeneration of deactivated catalysts (Neumann and Hicks 2012; Tamunaidu and Bhatia 2007; Williams and Chishti 2000; Chaube 2004).

The products from pyrolysis may include bio-oil, synthetic gas, and char (Boateng et al. 2006). Although thermal cracking of biomass into biodiesel and biogasoline may be costly, in situ upgrading and commercialization may help lower the operational costs thus presenting it an attractive technology in the future. Solantausta et al. (1994) have tested the feasibility of using pyrolysis oil (from sawmill wastes) in a diesel engine with a pilot injection system, which proved to be successful for a short-term use. Other researchers (Billaud et al. 1995; Jones et al. 2009) have also reported the success of using pyrolysis oil blended with PD (whose characteristics were close to those of biodiesel) in diesel engines.

One major problem associated with the direct use of vegetable oils and their blends with PD in diesel engines has been their high viscosity. Microemulsions of oils with alcohols, surfactants, PD, water (mostly as aqueous alcohol), as well as other solvents have been among the common technologies of reducing the viscosity of vegetable oils to be effectively used as fuels in diesel engines without major modifications. However, the problems of carbon deposits, injector needle sticking as well as high viscosity of microemulsions used in diesel engines continue to exist. Microemulsions are thermodynamically stable mixtures of immiscible liquids formed by the dispersion of fluids with optically isotropic microstructures of the fluids with diameters of 150 nm and mostly separated by surfactant films (Fletcher and Morris 1995). Water and alcohols have been the commonly used solvents sometimes blended with vegetable oils for microemulsions and used as fuels in diesel engines. Nguyen et al. (2010) have reported the successful use of water/oil microemulsions blended with PD in the ratio of 40 % in diesel engines without modification. Other studies (Lif and Holmberg 2006; Griffith et al. 1990; Flanagan et al. 2006; Goering et al. 1983) have also tested the possibilities of using water/oil and aqueous alcohol/oil (oils from palm, soybean oil, etc.) microemulsions blended with PD as fuels in diesel engines mostly in the ratio range of 5–95 % microemulsion/PD. These microemulsions have proven to possess good characteristics close to those of PD. Hunter (1996) has reported that improved microemulsion fuels are mostly prepared from about 70–99 % alcohol/fatty acid esters, about 1–30 % alcohol and less than 1 % alkali metal soap. Rao et al. (2012) have also successfully tested the use of microemulsions from alcohol and SVO with PD and rapeseed oil biodiesel blends in a diesel engines. They found out that their characteristics were highly comparable to those of PD. Alcohols such as 1-butanol, methanol, and ethanol have been tested to form good microemulsions with vegetable oils, which can be blended with PD and used in diesel engines. All these reports show success for only short-term use without major engine modification. However, long-term use of microemulsions in diesel engines still shows engine coking, injector needle sticking, and carbon deposits thus the need for process improvement in liquid biofuels production for sustainable development.

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[6] Commonly used catalysts for pyrolysis include silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), zeolites, clay montmorillonite, aluminum chloride, aluminum bromide, ferrous chloride, ferrous bromide etc.

Presently, the commonest commercial biodiesel production technology is the transesterification reaction (also known as alcoholysis) of the triglyceride of the fatty acid in the oil with alcohol (mostly methanol) catalyzed by a base or acid to produce mono alkyl esters (biodiesel) as main product and glycerin as co-product. This process is able to reduce the viscosity of the oil by a factor of eight; reduce the molecular weight of the oil to one-third that of the original weight and increase the volatility of the oil (Schwab and Bagby 1987). Again, transesterification is a simple process which produces biodiesel whose characteristics are very close to those of PD (compared to those produced from their other methods) and can be directly combusted in diesel engines without modifications with very low carbon deposits (Srivastava and Prasad 2000). In order to achieve sustainability in terms of biodiesel production via transesterification, there are many factors which need to be considered. For instance, the reaction time is dependent on the reaction temperature hence the catalysis may require high/low energy which may alter the sustainability of the biodiesel produced. Figure 2.2 shows the schematic flow diagram of a general transesterification reaction of vegetable oil/fats into biodiesel.

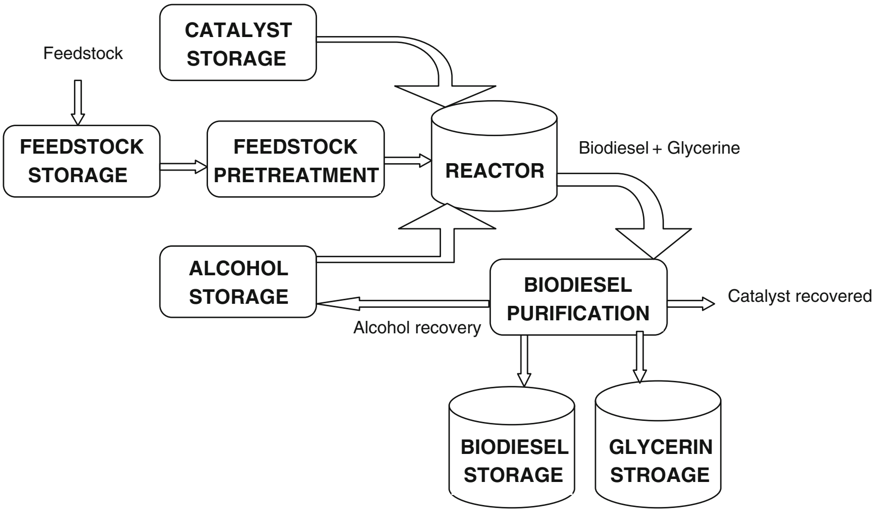

Fig. 2.2 Simplified process flow diagram for transesterification of vegetable oil/fats into biodiesel

Mono alkyl esters can be produced via catalytic, noncatalytic, and supercritical fluid transesterification reactions. Transesterification of oils and fats can be grouped into:

- Acid catalysis
- Alkaline catalysis
- Enzymatic catalysis

Catalytic Transesterification Methods

- Supercritical fluid transesterification – Non-catalytic transesterification reaction

Transesterification reaction can occur with or without the presence of a catalyst. However, catalysts are mostly used to increase the reaction rate hence shorten the reaction time and increase the biodiesel yield eventually. Catalytic transesterification reaction (acidic, basic, or enzymatic) may be either homogeneous or heterogeneous depending on the type of catalyst used.[7] Again, these catalysts may be in the form of liquid, solid, or gas with each having its own advantages and disadvantages. After heterogeneous catalysis, the catalyst and biodiesel exist in different physical phases and the possibility of separating them is high. This makes the whole reaction becomes simpler and cost-effective compared to homogeneous catalysis even though its reaction is highly selective (Deshpande et al. 2011). Many researches have investigated into the reaction conditions of transesterification of fats and oils from fish, soybean, rapeseed, sunflower, peanut, palm nuts, linseed, etc. (Saka and Kusdiana 2001; Lang et al. 2001; Mittelbach and Gangl 2001; Diasakou et al. 1998; Joelianingsih et al. 2008) using the various methods of transesterification reactions described above. Table 2.3 summarizes the basic differences between the main types of transesterification methods for biodiesel production.

2.3.1.2 Biodiesel Production and Consumption: Global Profile

Presently, biodiesel is the second most produced and consumed liquid biofuel (though diesel forms about 70 % of road transport fuel) in the world with Germany remaining the leading producer (from rapeseed and imported palm oil) due to the presence and enforcement of biofuel laws and subsidies policies (WWI 2006; EIA 2011). The common feedstocks used for biodiesel production in the world in 2011 are presented in Fig. 2.3.

Biodiesel is currently produced in commercial quantities by many companies like ADM Ölmühle Hamburg in Germany (using rapeseed oil), Diester Industrie in France (a capacity of about 3.5 billion liters of biodiesel using rapeseed and

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[7] Examples of homogeneous catalysts are sulphuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH) etc. Sulphated zirconium, K_2CO_3/MgO etc. are examples of heterogeneous catalysts used during transesterification reactions.

Table 2.3 Differences between the common types of transesterification methods used in biodiesel production.

Transesterification method	Pros and Cons
1. Acid catalysis	1. Catalyzed by Bronsted-Lowry acid (mostly sulphonic, sulphuric, hydrochloric and nitric acids) 2. Catalysts are corrosive, hazardous and expensive (yet more active) 3. Slow reaction requiring long time for completion[a] 4. High temperature requirement (depending on the type of alcohol) 5. High biodiesel yield (depending on the feedstock type) 6. Mostly accompanied by the formation of carboxylic acids which may reduce the yield and quality of the biodiesel produced. This can be avoided by carrying out the reaction in the absence of water
2. Base catalysis	1. Catalyzed by alkaline catalysts such as alkaline metal alkoxides (e.g., CH_3ONa) and hydroxides (e.g., KOH, NaOH), sodium or potassium carbonates, etc. 2. Catalysts are less corrosive and cheaper (yet less active) compared to acid catalysts 3. Faster reaction hence short time for reaction completion compared to that of acid catalysis 4. Requires low temperature 5. Low yield due to soap formation during the reaction
3. Enzymatic catalysis	1. Mostly catalyzed by free or immobilized lipase 2. Higher cost of enzyme makes the process expensive 3. The insolubility of methanol[b] and glycerin in oil inhibit the enzymes hence decreasing the catalytic activity of the transesterification reaction and the operational instability of the enzyme 4. Requires low temperature 5. High biodiesel yield
4. Supercritical Fluid	1. No need for catalyst 2. Technology is simple but cost ineffective due to high pressure and temperature requirements for the reaction to proceed. 3. Shorter reaction time. 4. Higher yield (i.e more efficient method) compared to the catalytic transesterification methods 5. Easier purification of products 6. Heavy use of fluid for reaction hence increasing raw material cost.

[a] Depending on the type of alcohol used, the reaction time may differ (between 6 and 50 h). For instance, for the same amount of alcohol and acid catalysts, transesterification with methanol, ethanol and butanol may take 6–50, 18 and 3 h respectively (Bhatti et al. 2008)

[b] Other solvents such as n-hexane and petroleum ether have also been reported to exhibit the same problem associated with methanol in enzyme-catalyzed transesterification unlike *n*-butanol, a tertiary alcohol, which is not a substrate for lipases (Shimada et al. 2002; Li et al. 2006)

sunflower oil), GlobalFuel Technologies Corporation (using algae), PetroSun Biofuels Inc. in the USA (a capacity of about 114 million liters of algal biodiesel), Global Green Algae in the USA as well as Biodiesel-Oil-Fujian Zhongde Energy Co. Ltd. in China (a capacity of about 117 million liters of straw oil biodiesel), Gushan Environmental Energy Ltd. in China (a capacity of about 222 million liters

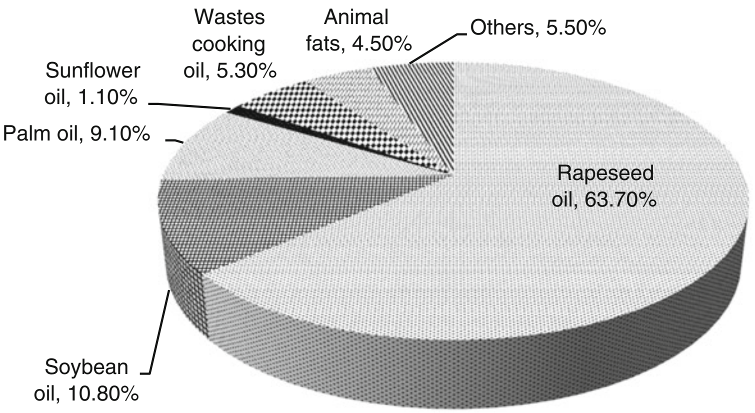

Fig. 2.3 Percent share of feedstocks used for biodiesel production in the world in 2011 ('Others' include non-edible energy crops, bio-oils, etc.)

of biodiesel from used/waste cooking oil), Solazyme in the USA (a capacity of about 114 million liters of producing bio-oil from algae), etc. Algae fuels used as jet fuels and biodiesel are produced by other companies like USA-based Chevron Lummus Global and Aemetis (with a total capacity of about 398 million liters annually in the USA and India). Solazyme Company is set to increase their production capacities and be on the biofuel market by the end of 2013 with a production cost target of US$ 60–80 per barrel (GigaOM Report 2012). Neste Oil, a BtL production company in Finland is currently using NexBtL process, which is similar to the Fischer–Tropsch process in converting biomass into biodiesel.[8]

A capacity of over 2.1 million tons of BtL production plants are currently in operation in various parts of the world with Singapore, Finland, and the Netherlands accounting for the largest share (about 1.94 million tons) in capacity (Honkanen 2008). Sapphire Energy in the USA is currently one of the biofuel companies in the world with very high production capacity and produces a fourth generation algal bio-oil whose total production capacity is set to hit about 5.7 million liters by 2014 (Honkanen 2008).

In 2008, the global total biodiesel production capacity was 11 million tons which increased to about 21 million tons in 2010 and projected to reach about 84 million tons by 2016, with an annual average growth rate of over 30 % (IEA 2010; EIA 2011). All over the world, biodiesel is consumed at a rate of 3.8 million tons per year and this is also projected to reach about 28 million tons by 2015 (IEA 2010).

These statistics clearly indicate that there is a high possibility of biodiesel contributing as much as 20 % of the world's total capacity of all on-road diesels by 2020. Biodiesel is mainly produced from palm oil in Malaysia, Indonesia, and

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[8] The BtL products (biodiesel and bio-gasoline) produced from palm oil via the NexBTL process are found to have greenhouse gas emissions of about 40–60 % (over its entire life cycle) lower than that for fossil fuel (Hodge 2006).

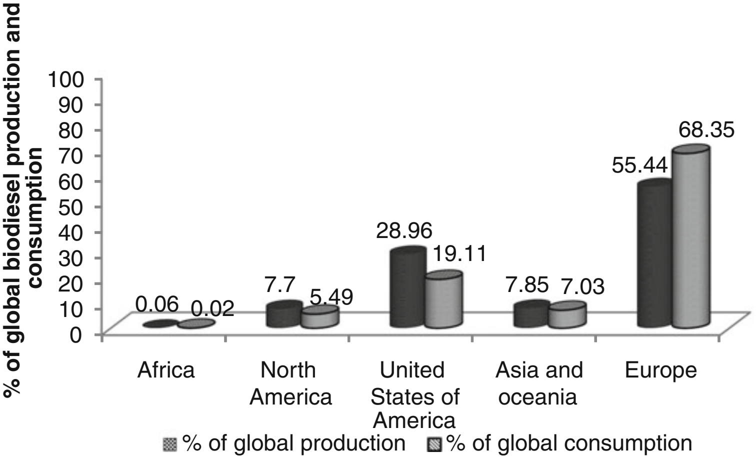

Fig. 2.4 Regional contribution of biodiesel production and consumption to the world's capacity in 2010 (IEA 2010)

Thailand, and other parts of Asia with total palm biodiesel production of about 31.4 million tons annually (Shrestha and Gerpen 2010). As at 2010, the total installed biodiesel production capacity in Malaysia for instance was about 2.7 million tons with active production capacity of about 170,000 tons (MPOB 2010; Lim and Teong 2010). In 2011, about 12 biodiesel production plants (out of the 60 plants with capacity 3.37 million tons which were licensed by the Malaysian government) were actively involved in the production of palm biodiesel contributing about 117,000 tons to the world's capacity (MPOB 2010). In Malaysia, at present, only about 1 % of its palm oil is used to produce biodiesel, whereas Indonesia uses about 9 % of their palm oil for biodiesel production. In 2011, Malaysia exported about 50,000 tons (about 42.7 % of their total production) of biodiesel, which was a drop from about 86,000 tons (about 50.6 % in 2010) bringing in only about RM 266.58 million (MPOB 2010). However, the demand for biodiesel in 2011 was about 200,000 tons. In order to encourage the sustainable production and consumption of biodiesel in Malaysia, the government has provided subsidies of RM 0.05–0.07/l of biodiesel. In the EU, biodiesel production from rapeseed oil was estimated to cost over 3 times higher as that for PD in 2007 (OECD-FAO 2011). In Germany, excise tax exemptions have been driving the demand for biodiesel whilst in the USA, a federal subsidy of US$ 0.26/l as well as state incentives make the biodiesel market attractive. Figures 2.4 and 2.5 show the regional and global biodiesel production and consumption in 2010, respectively (IEA 2010). From Fig. 2.5, it could be seen that the total biodiesel production and consumption capacities kept increasing from year to year thus the need to adopt sustainability practices in order to achieve the beautiful benefits of biofuels in future.

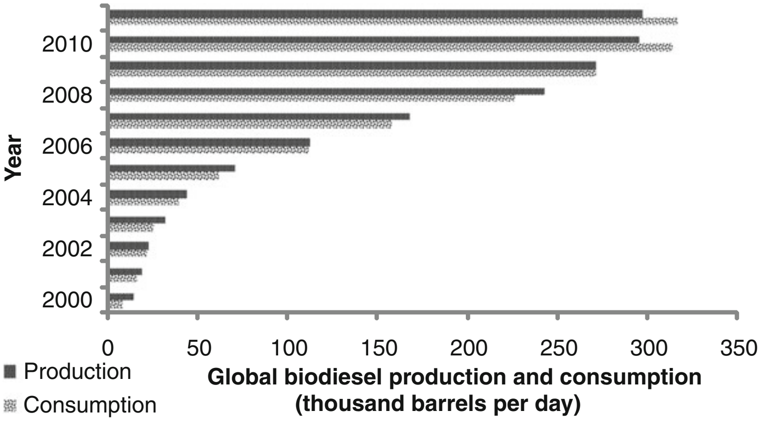

Fig. 2.5 Global biodiesel production and consumption (IEA 2010)

The major feedstock contributors to global biodiesel production over the years have been rapeseed oil (in the EU), soybean oil (in the USA) and palm oil (in Asia) with global contributions of 27, 17, and 10 %, in 2010; respectively (MPOB 2010). Jatropha biodiesel has also gained much interest in India and some parts of Asia with minimal contributions presently. The estimated capacity for biodiesel production by 2015 demands large acres of land for feedstock cultivation which would in fact surpass the available global land hence the need for research and developments for second-, third-, and fourth-generation feedstocks for biodiesel production.

Though the EU represents more than half of the global production of biodiesel presently, it is projected that Asian countries like Malaysia and Indonesia may come closer by 2020 as their markets are expanding at faster rates. By the year 2020, it is estimated that biodiesel would represent about 20 % of all on-road diesel fuels used in the world when tax incentives, research and development as well as other sustainability standards are realized in the shortest possible time (IEA 2010). In the EU, in 2011, about 171,000 barrels and 217,000 barrels per day were produced and consumed respectively representing about 6 % of the total on-road diesel fuels in the EU (EIA 2011). By the end of 2005, the EU had achieved their target of 2 % biodiesel contribution to their total on-road diesel fuels. These figures are believed to increase drastically for the next decade if feedstocks become highly available and government subsidies continue to be implemented. In the USA, it is mandated under its Renewable Energy Standard that all cars must run on biodiesel and bioethanol (and their blends with PD) by 2020. Under this law, presently about 3 % of all smaller cars, over 80 % of all commercial trucks and buses run on biodiesel. Apart from the EU and the USA, China, India, and Brazil have also emerged as big markets for biodiesel over the last 5 years (EIA 2011).

2.3.2 Bioalcohols

Bioalcohols are one category of liquid biofuels that are produced from carbohydrate materials. Alcoholic fuels have the chemical formula $C_nH_{2n+1}OH$. Bioalcohols mostly used as fuels include the first four aliphatic alcohols, namely, methanol, ethanol, propanol, and butanol because they can be easily synthesized to be used in engines due to their high octane rating, which increases fuel efficiency and lowers the energy density of fuels compared to gasoline. Bioalcohols have the potential to reduce the emissions of nitrogen oxides (NO_x), carbon dioxide (CO), and nonmethane hydrocarbons (NMHC) by 25–32, 12–24, and 20–22 %, respectively compared to conventional gasoline (CDIAC 2010).

Feedstocks for bioalcohol production consist of mainly cellulose and holocellulose (hemicellulose and lignin), which are mostly broken down by enzymes, heat or chemicals through various processes. First-generation bioalcohols are produced from sugar and starchy materials such as cassava, cereals (e.g., sugar beet, wheat, etc.), sugarcane, etc. Second-generation bioalcohols (also called cellulosic alcohols) are also produced from cellulosic biomass such as agricultural wastes (e.g., leaves, straw, etc.), forest residues, municipal solid organic wastes, and industrial solid wastes (e.g., sawdust, sugarcane bagasse, etc.). The conversion technologies for lignocellulosic materials into second-generation bioalcohol are sophisticated though the feedstocks are cheaper compared to the FGF. Also the growth of SGF is found to be potentially invasive thus bound to have negative impacts on biodiversity. Nonetheless, bioalcohols produced from SGF can produce greater amount of biomass per hectare of land and most of the feedstocks can grow well on marginal lands where food crops cannot.

2.3.2.1 Bioalcohols Characteristics and Production Technologies

Biomethanol (also called methyl alcohol, methyl hydrate, or wood alcohol) is the lightest, simplest, and less energy-rich bioalcohol that may be produced from synthesis gas (syngas or methane) through gasification, electrolysis or enzymatic conversion of biomass into hydrocarbon rich gas (syngas), which is further converted into biomethanol. Because the technology for producing biomethanol requires large quantities of biomass as feedstock, they are economically feasible when available in large quantities. Biomethanol is found to be the most cost-effective and environmentally friendly liquid biofuel for fuel cell vehicles. The first commercial biomethanol production plant in the world is in operation in Sweden and it produces about 300 tons of biomethanol per day ($\sim$74 MW) .

Bioethanol is by far the most produced and consumed liquid biofuel in the world mostly obtained from FGF such as corn/maize, beet, sugarcane, wheat, etc. In countries like Brazil, North America, and France, bioethanol (also called ethyl alcohol) is mainly produced from sugarcane, corn/maize, and sugar beet, respectively with Brazil, the USA, and China being the top producing countries (OECD-FAO 2011). Unfortunately, the use of these FGF for bioethanol production directly compete with food for land thus countries like Malaysia and Indonesia are working hard to commercialize second-generation bioethanol production from lignocellulosic materials from solid palm wastes like oil palm fronds. Other disadvantages of bioethanol use may include its ability to be contaminated easily with water compared to gasoline; its corrosiveness; sophisticated production technology (when using lignocellulosic materials as feedstock), etc. Though some studies reveal that bioethanol has lower energy output compared to its energy inputs making them economically unsustainable, Shapouri et al. (2002) and Kim and Dale (2002) have produced a contradictory report. However, apart from bioethanol production from FGF such as corn bringing up the issue of land competition with edible crop production, the technology is simple and cost-effective. On pilot and laboratory scale, bioethanol is commonly produced by the method of separate hydrolysis and fermentation (SHF) using enzymes suitable to completely convert the particular type of feedstock into bioethanol. Hydrolysis is a chemical reaction that converts complex polysaccharides (e.g., starch, cellulose, chitin, glycogen, etc.) in biomass into simple sugars (i.e., monosaccharides) such as glucose (dextrose), galactose, fructose, hexose, xylose, ribose, etc., which is commonly catalyzed by enzymes, acids, and alkaline. Fermentation, on the other hand, converts the simple sugars from the hydrolysis reaction into bioethanol (with carbon dioxide as by-product) with the help of yeast (mostly *Saccharomyces cerevisiae)*. Recently, simultaneous saccharification and fermentation (SSF), which employs both the hydrolysis and fermentation of the pretreated feedstock in one reactor, has emerged as a cost-effective method. The utilization of lignocellulosic waste materials may present a more economical way of producing bioethanol commercially if the technology is appropriately developed and accordingly optimized.

Bioethanol has been used extensively as gasoline substitute in most parts of the world. Like biodiesel, bioethanol characteristic performances in gasoline engines are markedly improved by blending with gasoline. Globally, the commonly used bioethanol blends are E10 (10 % bioethanol, 90 % PD), E15 (15 % bioethanol, 85 % PD), and E20 (20 % bioethanol, 80 % PD). Other high level blends such as E85 (85 % bioethanol, 15 % PD), E95 (95 % bioethanol, 5 % PD) have also been used as transportation fuels in the USA, Australia, and Brazil. The high octane rating of these bioethanol blends makes them less prone to knocking (i.e., a rattling or pinging sound that results from premature ignition of the compressed fuel–air) thus improving the energy efficiency of the vehicle's engine for better fuel economy.

Though methanol and ethanol can be produced from fossil fuels or carbon dioxide and hydrogen, they can easily be synthesized from biomass (sugar) by fermentation using enzymes or other chemicals at much cheaper costs relative to those produced from carbon dioxide and hydrogen. The energy contents of bioethanol, biomethanol and gasoline are 21.1, 15.8, and 32.6 MJ/l fuel, respectively (Larson 2008). Bioethanol is less corrosive and less toxic compared to biomethanol and gasoline.

Biobutanol is also another type of bioalcohol, which is not commonly produced due to its complex production technology. Biobutanol is chemically produced from the fermentation (also called acetone-butanol-ethanol (ABE) or solvent fermentation) of biomass using enzymes such as *Clostridium acetobutylicum* and can be used directly in gasoline engines without major modifications. During the ABE fermentation process for biobutanol production, co-products like butyric, propionic and acetic acids are initially formed with the help of the enzyme. Other metabolic activities occur within the fermentation broth which produces butanol, acetone and ethanol (Fond et al. 1985; Qureshi et al. 2002). Biobutanol has high octane rating (85) which is very close to that of gasoline (87) and also has high energy density (29.2 MJ/l) compared to those of bioethanol and biomethanol. Biobutanol, in particular, has its energy density so close to that of gasoline but its production technology is difficult to optimize and still under research and development. However, the high flash point of biobutanol of 35 °C (though a good point for fire safety, it is not suitable for use in cold weather), high toxicity and high emissions of odoriferous substances make them less advantageous compared to biomethanol and bioethanol. Biobutanol can be blended in small quantities with gasoline and used in an unmodified gasoline engines (though some may not be compatible with biobutanol) as its air to fuel mixture ratio (11.2) is close to that of gasoline (14.7).

Presently, there is no vehicle running on 100 % biobutanol apart from few of them which run on its blend (up to 10 % biobutanol) with gasoline (Mansur et al. 2010). Biobutanol is considered accepted for use in diesel engines when its purity is $\geq$99.5 % and contains $<$0.5 % water and $<$0.01 % ketones and aldehydes (Mansur et al. 2010). This is indeed difficult specifications to achieve due to the fact that there exists an azeotrope of 94 % purity, which needs to be dealt with during butanol production (Mansur et al. 2010). Because it can produce high voltage compared to the other bioalcohols, they are used as sources of hydrogen in fuel cells, though less preferable, due to the difficult biomass conversion technology into the alcohol.

Biobutanol is mostly produced by fermentation of the biomass with bacteria (often *Clostridium acetobutylicum or Clostridium beijerinckii*) to obtain acetone, butanol, and ethanol depending on the process conditions. Unlike bioethanol, biobutanol is resistant to water contamination and safe to handle and transport at high temperatures due to its low vapor pressure compared to gasoline. However, biobutanol on combustion may release more toxic substances or emissions compared to gasoline and presently, the commercial production of biobutanol may not be cost-effective (especially with the distillation process to obtain the biobutanol due to its low concentration in the fermentation broth as a result of product inhibition) compared to that of conventional butanol. Phillips and Humphrey (1983) have investigated the economic analysis of biobutanol recovery through distillation. Their report showed that for efficient energy use in the biobutanol production plant, the concentration of the biobutanol in the fermentation broth must be at least 25 g/l which is in fact difficult to achieve. As reported by Ramey and Yang (2004), biobutanol concentration of 20 g/l, productivity of 4.5 g/l h, and yield of $<$25 % w/w from glucose have been the best results so far. Other energy recovery methods such as

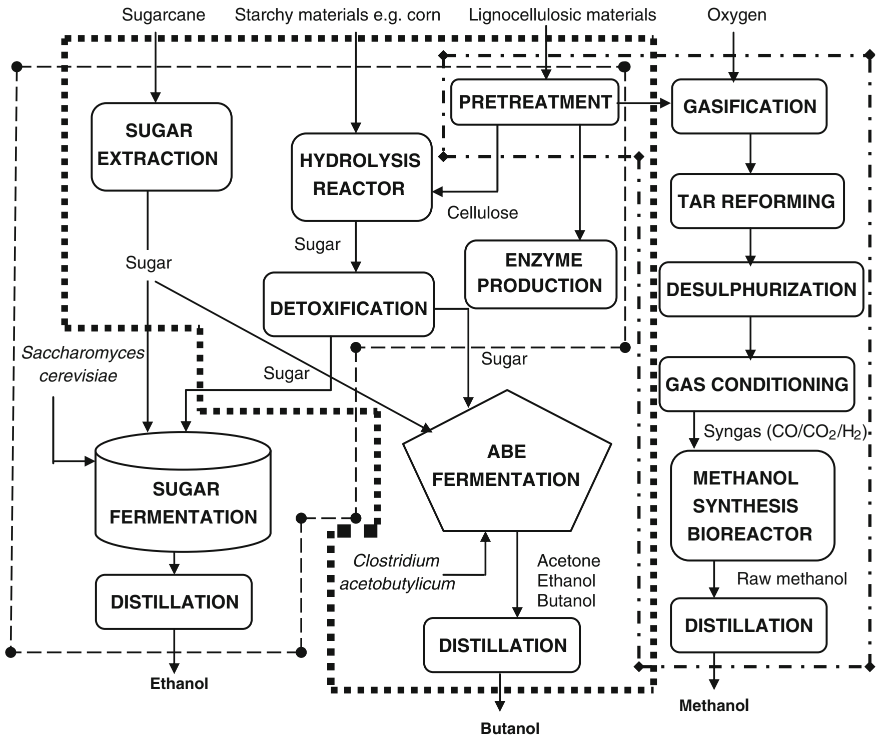

Fig. 2.6 Schematic flow diagram of bioalcohol production from different feedstocks (■ ■ ■ ■ ■ ▮, ●– – – –●, ◆– · – · –◆, represent biobutanol, bioethanol, and biomethanol production plants, respectively)

in situ gas stripping, liquid–liquid extraction, reverse osmosis, etc., could be developed and applied for sustainable production (Groot et al. 1992; Chauvatcharin et al. 1998; Ezeji et al. 2003; García et al. 2011). Unlike biomethanol, bioethanol, and biobutanol, biopropanol is not commonly used directly in gasoline engines as fuel but mainly used a solvent. Figure 2.6 describes in brief the process flow of the simultaneous production of types of bioalcohols from biomass.

2.3.2.2 Global Statistics of Bioalcohols Production and Consumption

The greatest volume of liquid biofuels produced and consumed in the world presently is bioethanol produced from wide range of feedstocks with about 80 % sourced from corn and sugarcane together. Presently, bioalcohols are produced from FGF such as corn, barley, oats, rice, wheat, sorghum, sugarcane, etc., mostly in Brazil and the USA. Asia is the leading producer of sugarcane (159 million tons annually) followed by the USA (121 million tons annually) with Brazil being the

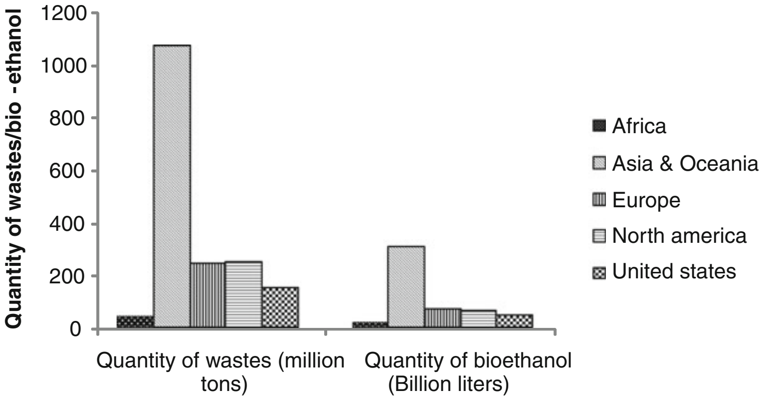

Fig. 2.7 Availability of lignocellulosic wastes for bioethanol production (IEA 2010)

largest single producer accounting for about 98 million tons annually. Out of these production statistics, only about 2 % are used to produce fuel ethanol (OECD-FAO 2011). From 2002 to 2007, the cost of grains in the USA was about 30 % higher due to the production of corn mainly for bioethanol production. By the end of 2007, about 25 % of the total amount of corn produced in the USA was converted to bioethanol (Trostle 2008). All over the world, with the exception of North America, Oceania, and Europe, about 3.3 million tons of sugarcane (which could produce about 1.6 billion liters bioethanol) produced annually go to wastes.

The lignocellulosic wastes obtained after harvesting and pretreatment of these FGF are abundant yet only a few bioethanol production plants that convert these wastes into cellulosic ethanol are commercialized presently due to sophisticated technology involved. All over the world, the major lignocellulosic feedstocks for bioethanol production are abundant (about 1.7 billion tons) especially in Asian countries with the main components being palm wastes, wheat straw, and rice husks (OECD-FAO 2011). In order to achieve bioethanol production sustainability, these wastes referred to as SGF could replace the FGF, which are currently used to produce bioethanol. Figure 2.7 shows the availability of lignocellulosic feedstocks and their potential amount of bioethanol obtained from them in the five regions of the world.

Of all the types of bioalcohols, bioethanol is the most produced in the world presently with North America and the USA dominating and accounting for more than 90 % of the total production capacity. According to the report issued by the Civil Aviation Administration of China (2012), China is the third largest producer of bioethanol, and it is set to reach about 14 billion liters of aviation biofuel by 2020. In 2006, India also contributed about 4 % of the global total bioethanol production and by 2015, they plan to replace about 10–20 % of gasoline by bioethanol. Since 2000, there has been consistent increase in bioethanol production and consumption rate with annual growth of about 6–12 % worldwide (IEA 2010; OECD-FAO 2011).

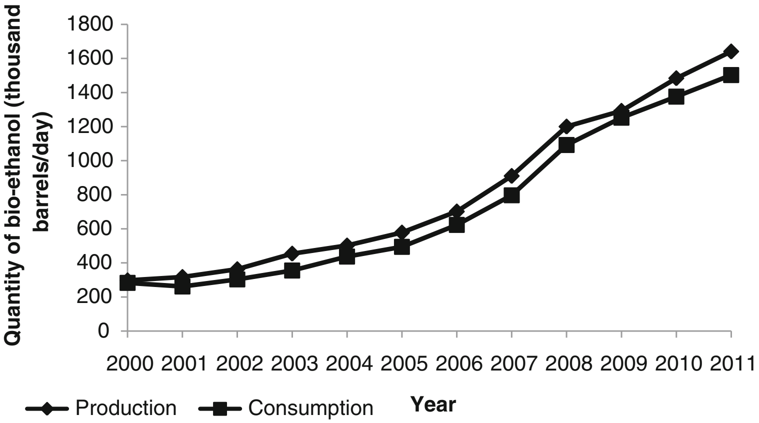

Fig. 2.8 Global bioethanol production and consumption trends from 2000 to 2011

From 2000 to 2007, the world's total bioethanol production had increased three folds due to attractive government incentives in most producing countries. In 2009 and 2010, the global total quantity of bioethanol produced for fuel purposes were about 89 billion liters and 93 billion liters, respectively with consumption capacities of 63 billion liters and 79 billion liters, respectively (OECD-FAO 2011). The consumption rates in Asia and Africa decreased in the year 2009 by about 4 and 80 %, respectively and drastically increased in 2011 by about 13 and 26 %, respectively (OECD-FAO 2011). Figure 2.8 shows the global trend in the production and consumption of bioethanol from the year 2000 to 2011. In 2011, the world recorded a total production of about 99.8 billion liters of bioethanol with about 90 % being consumed as fuel (OECD-FAO 2011; EIA 2011). Presently, the North America holds the greatest share of bioethanol market (about 63 % of the world's bioethanol market) followed by the USA with a share of 31 % of the total world's market (EIA 2011). Although Asia and the Oceania together contribute only about 3 % of the world's market presently, they hold promising future than the EU, which has a share of about 2.7 % (OECD-FAO 2011; EIA 2011). Figure 2.9 shows the regional shares of bioethanol production and consumption in the year 2011.

It was predicted that by the end of the year 2012, Brazil and the USA would have increased their bioethanol production capacity to about 19 million liters (about 20 % their current production) and 30 million liters (about 43 % their current production), respectively (EIA 2011). These regions hope to expand their production, consumption, and market capacities by the year 2020. Globally, whilst the cost of production of a liter of bioethanol is about US$ 0.22 and US$ 0.30 in Brazil and the USA, respectively, it is sold at about US$ 0.53 on the international market (RFA 2010). The difference in prices is as a result of the type of feedstock used. Brazil uses sugarcane, which does not need any pretreatment whilst the USA uses corn which needs some hydrolysis before further fermentation into

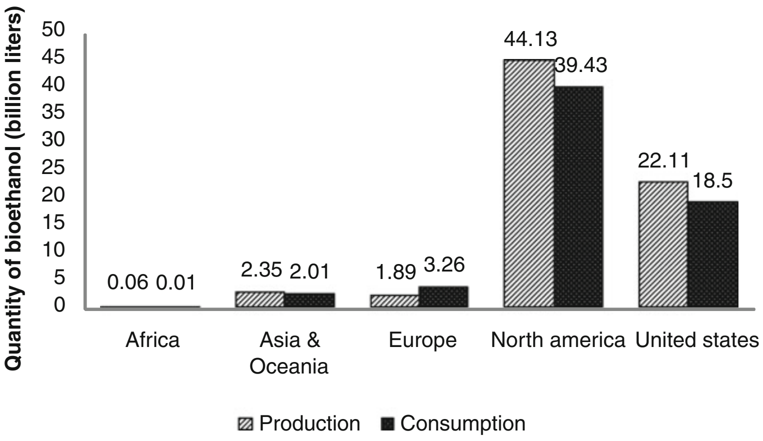

Fig. 2.9 Regional share of bioethanol production and consumption in 2011

bioethanol. Improvements in the technologies for bioethanol production as well as the use of the appropriate feedstock may render the fuel cost-effective in the near future.

In most parts of Europe and the USA, biofuel blending directives have been implemented. For instance in Sweden, gasoline is to be substituted by about 500 million liters of bioethanol every year. The largest biomethanol production plant in the world, which is located in Sweden (Värmlands Metanol AB) produces about 130 million liters of fuel grade biomethanol to replace gasoline. Throughout the world, there exists over 500 bioethanol production plants utilizing various feedstocks with most of them based in Brazil and the USA and these plants are able to contribute over 150 billion liters of bioethanol annually (REN21 2010). In the USA, large capacity bioethanol production companies like LS9 Inc. (which produces bioethanol from sugarcane), DuPont Danisco Cellulosic Ethanol LLC (a capacity of about 104 million liters of bioethanol from nonedible plants),[9] Algenol (with a patented technology for bioethanol from photobioreactor grown algae), etc., are on commercial scale production. Chemrec AB, the first and largest biomethanol (164 million liters per year) and biodimethyl ether (DME) (117 million litres per year) production plant in the world is based in Sweden, which uses black liquor from pulp and paper mills as their major feedstocks (EIA 2011).

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[9] DuPont Danisco Cellulosic Ethanol LLC is set to begin operation in 2013. Presently, there is no company in the world producing commercial cellulosic bioethanol. However, companies like Novozymes, Diversa, Dyadic in the USA are currently developing efficient enzymes for the conversion of lignocellulosic materials into bio-ethanol. Again, in USA and some parts of Asia, over 20 companies have been testing their technologies on pilot scale since 2008 with the hope of commercializing by 2017 (Fehrenbacher 2012).

2.3.3 Other Liquid Biofuels (Bio-oils)

Bio-oil is a black liquid residue obtained from biomass hydrocracking and pyrolysis processes (Fig. 2.1). It has low energy density of about 17 MJ/kg than gasoline (about 39 MJ/kg) but high energy density compared to that for wood chips (about 4.5 MJ/kg) and straw (about 1.1 MJ/kg) (Lang et al. 2001; Akhtar and Amin 2011). With or without the addition of surfactants to bio-oils, they are very low in minerals and sulfur thus an attractive substitute for gasoline. Bio-oils are often used as boiler fuels and sometimes pretreated and combusted in diesel engines and turbines to generate electricity (Easterly 2002).

Apart from biodiesel and bioethanol, liquid biofuels such as pure plant oil (PPO) or SVO are common as fuels that are used in diesel engines in some parts of the world including the USA and the EU. PPO is produced by cold pressing of oil crops such as rapeseed, *Jatropha curcas L.*, moringa, palm fruits which have successfully being used in diesel engines without modifications though they have high freezing points. Second-generation PPO (produced from SGF like *Jatropha curcas L*, karanj, etc.) are more sustainable compared to first generation ones that are produced from food crops. In some countries such as Finland and Singapore, SVO or animal fats are hydrogenated to form another important liquid biofuel, which is also used in diesel engines.[10]

Biokerosene is another liquid biofuel produced from oil seeds (by hydrogenation of the oils and liquefaction of gasified biomass), which is common in most rural parts of the world where electricity is not reachable. For instance, in developing countries such as Ghana, Tanzania, etc., *J. curcas* oil has been used as biokerosene in lamps as source of lighting in rural areas (Ofori-Boateng and Lee 2011). Rarely, biokerosene is used in aviation sectors to fuel jet engines due to its low freezing point and energy density (43.1 MJ/kg).

Pyrolysis oil also called bio-oil is the main product from the pyrolysis of biomass, which has been used as substitute for PD. Like tar, pyrolysis oil contains high levels of oxygen (40–50 %) thus slightly different in chemical characteristics compared to petroleum fuel hence not commonly used in fuel systems. Though the properties of pyrolysis oil depend on the kind of feedstock used, generally, they are acidic (pH of 2.7) and contain about 20–25 % water and 20–36 % sediments Sadaka and Boateng (2009) with lower heating value of 18.5 MJ/kg, flash point of 40–100 °C, pour point of −12 to −33 °C and cetane number of 10.

Pyrolysis oil usually cannot be easily blended with PD thus need special engine modification before use in its pure form in engines. For pyrolysis oil production processes to be more sustainable, the valuable components of the oil could be isolated and then the oil combusted to generate electricity or converted to syngas (Akhtar and Amin 2011).

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[10] This technology has not been tested on commercial basis yet (Bacovsky et al. 2010).

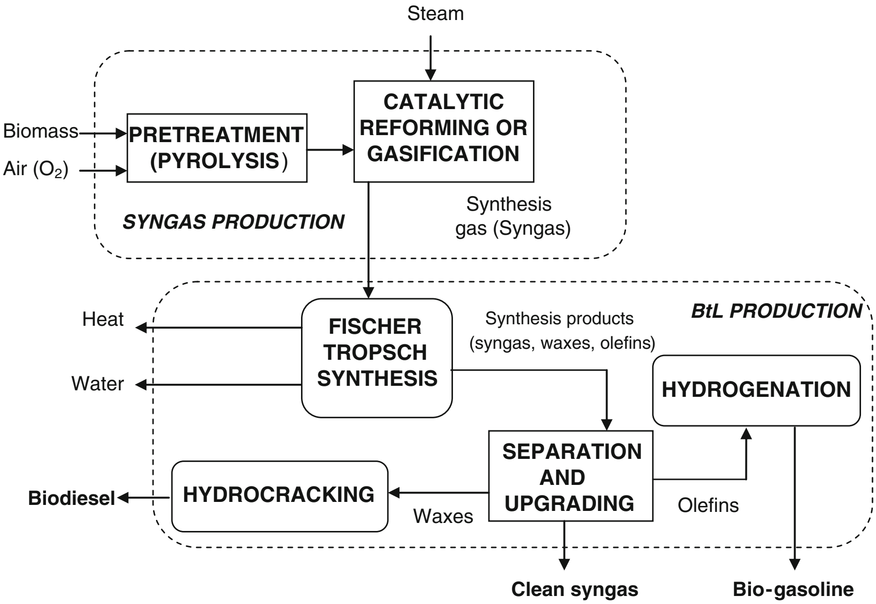

Fig. 2.10 Simplified flow diagram of BtL production process via the Fischer–Tropsch process

Biogasoline is also a type of liquid biofuel produced from algae biomass and cellulosic feedstocks like oil palm fronds, oil palm empty fruit bunches, switch grass, etc., through thermochemical processes (Fig. 2.1) such as pyrolysis.

Bio-Ethyl-tertiary-butyl-ether (ETBE) is also another type of liquid biofuel mostly synthesized from bioethanol and isobutylene in a catalytic reaction. It is mostly blended with gasoline in any proportion up to 15 % to improve its combustion properties before use in car engines. Bio-ETBE is found to be more compatible with engines than bioethanol, and it is mostly used in conventional vehicles and fuel distribution systems in the EU.

Gasification of biomass into syngas and then conversion into liquid biofuels (like biomethanol and biodiesel) by the Fischer–Tropsch process (also called the biomass-to-liquids technology, BtL) has been used to produce diverse liquid biofuels.[11] Unlike the fermentation of biomass into bioalcohols, BtL generates many potential compounds that are substitutes for liquid biofuels and other biochemicals. BtL products mainly produced from agricultural or forest wastes are more environmentally friendly with high GHG savings compared to those from grown energy crops like miscanthus (Jungbluth et al. 2007). Figure 2.10 shows a simplified flow diagram of BtL production process via the Fischer–Tropsch process.

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[11] Biomass-to-liquid (BTL) biofuels also called Fischer–Tropsch fuels include synthetic diesel, bio-kerosene etc.

2.4 Gaseous Biofuels for Transport, Heat and Power Generation

Gaseous biofuels can be grouped into five, namely, biogas (commonly called biomethane), synthesis gas (biosyngas), synthetic natural gas, biopropane, and biohydrogen. They are mostly produced from feedstocks like sewage, animal waste, grass, leftover food, etc., through various processes such as anaerobic digestion (biochemical process), gasification (thermochemical process), etc. Gaseous biofuels are mostly characterized by their physical properties and chemical compositions based on the source of feedstock.

2.4.1 Biogas (Biomethane)

Biogas is a type of gaseous biofuel which comprises mainly methane (CH_4) and carbon dioxide (CO_2) as well as traces of hydrogen sulfide gas (H_2S), water, and siloxanes. It is commonly generated through the biodegradation of organic matter such as animal wastes, municipal wastes, industrial effluents, dead plant materials, energy crops, etc., in the absence of oxygen via a biochemical process. Depending on the type of feedstock and technology used for the biogas production, it can be alternatively called swamp gas, marsh gas, landfill gas, or digester gas. In most parts of the world, digester biogas is produced from animal wastes, organic industrial effluents, and food wastes. For instance, the dung from a cow could produce about 3 kWh electricity in a day, which is more than enough to power a 100 W light bulb which uses 2.4 kWh in a day. The calorific value of biogas is between 21 and 25 MJ/m^3 implying that for 1 m^3 of biogas, 1.7 kWh[12] electricity could be generated (Zhu et al. 2009).

One positive environmental impact of capturing biogas from cow manure other than allowing them decomposing without biogas capture is the reduction of global warming gases by 99 million tons or 4 % (Webber and Amanda 2008). For economic and environmental sustainability for the biogas production plant, biogas produced from byproducts of vegetable oil extraction and ethanol production as well as industrial effluents should be highly preferable.

Anaerobic digestion comprises four major processes, namely, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Bacterial hydrolysis decomposes the carbohydrates, fats, and proteins in the feedstock into sugar, fatty acids and amino acids, respectively. The products are then converted into carbon dioxide, hydrogen, ammonia, and other organic acids by acidogenic or fermentative bacteria.

The generated organic acids are further converted into acetic acid by acetogenic bacteria and finally, methane and carbon dioxide are formed as main products from

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[12] An energy content of about 6 kWh is assumed (corresponding to about 0.6 l of diesel fuel).

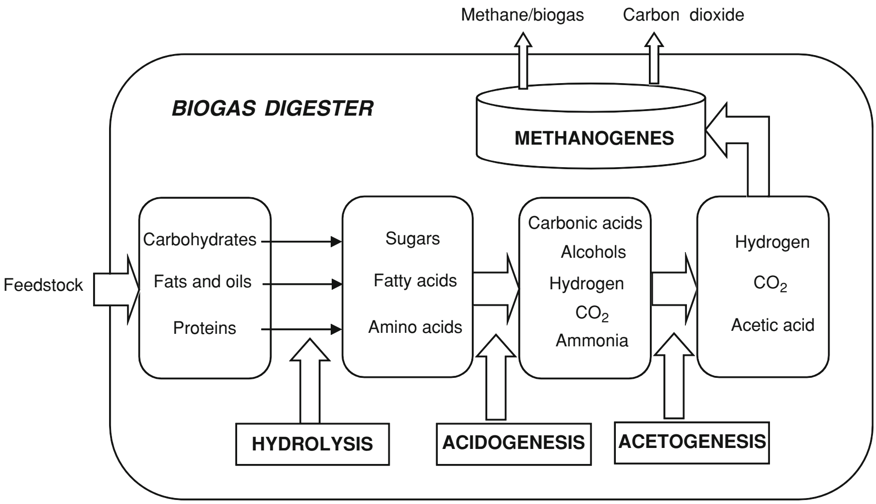

Fig. 2.11 Simplified process flow diagram of biogas production via anaerobic digestion

methanogenic bacteria (Song et al. 2004). These processes (especially the methanogenesis process) occur under controlled temperature, pH and pressure in order to attain the right kind of gases. The bacteria aiding the digestion could be mesophilic[13] or thermophilic.[14] The remaining residue or effluent from the digester can be used as organic fertilizer. Figure 2.11 shows the process flow diagram of biogas production from anaerobic digestion.

On the other hand, landfill gas is produced from wet organic wastes which decompose under anaerobic conditions with the help of bacteria in landfills either engineered or not. In an engineered landfill plant, the gas which is built up from the decomposed feedstock is captured, purified, and burnt in engines to generate bioelectricity. Landfills without gas recovery units may pose environmental problems as the methane generated from the site may contribute to global warming.

Presently, about 30 % of the biogas produced in the EU comes from sewage sludge and about 40 % originates from landfills. Before biogas could be transported or used in cylinders in cars, etc., they need to be purified. Water scrubbing technologies for biogas purification has been found to be one of the effective methods of rendering biogas compressible to be used in metal cylinders (Ofori-Boateng and Kwofie 2009). This technology is currently under application in Sweden where a 600 m^3/h water scrubber is able to purify biogas produced by the Henriksdal sewage water plant in Stockholm.

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[13] Mesophilic microorganisms are the bacteria that aid anaerobic digestion and usually thrive well between temperatures of 20–45 °C and pH of 7.

[14] Thermophilic bacteria operate efficiently at temperatures between 45 and 71 °C and pH between 2.3 and 5.

Generally, biogas is composed of about 50–75 % CH_4, 25–50 % CO_2, 0–10 % nitrogen gas, 0–1 % hydrogen gas, 0–3 % H_2S and negligible amount of oxygen, water vapor, ammonia, mercaptans, and other noxious gases (Zhu et al. 2009). However, the methane content could be increased to 80–90 % using advanced wastes treatment technologies with in situ gas purification unit (Richards et al. 1994). The calorific value of biogas is about 23 MJ/Nm^3, which is about half that for natural gas. The energy in biogas is released upon combustion or oxidation with oxygen molecules in gas engines and can be used as fuel for the production of heat and electricity (Richards et al. 1994). In some parts of the world like United Kingdom, biogas is purified, compressed, and used in motor vehicles or stored in gas cylinders just like liquefied petroleum gas (LPG). In the USA, the use of biogas for electricity generation forms about 3 % of its total electricity expenditure. In most developing countries in Africa and Asia, biogas is mainly used as fuels for cooking and rural electrification. Though the efficiency of directly converting biogas to power and electricity through gas engines is low (about 20 %) compared to its use for heat supply and district heating (about 60 %), biogas is still used for power generation in most parts of the world. Apart from the commonly used application of anaerobic digesters for biogas production, landfills are also designed to produce biogas, which can be captured for use. Biogas can be used in a combined heat and power (CHP) gas engines for cooking and heating applications.

2.4.2 Biosynthesis Gas (Bio-syngas)

Bio-Synthesis gas, also known as biosyngas or bioproducer gas is an intermediate gas (produced together with hydrocarbon liquid and char) which comprises carbon monoxide and hydrogen (as main combustible components) that is produced by the thermochemical gasification of biomass (Maschio et al. 1994). Biosyngas has its energy density almost half that of natural gas hence used as transportation fuels. Biosyngas can also serve as a feedstock for the synthesis of synthetic natural gas, biomethanol, bioethanol, dimethyl ether, etc. The combined processes of gasification, combustion, and pyrolysis of biomass in a controlled manner could result in the formation of biosyngas, which can be combusted directly in internal combustion engines to generate electricity and heat.

Biosyngas can be produced from biochar (Chaudhari et al. 2003), bio-oil (Panigrahi et al. 2003) or steam reforming of biogas from gasification process (Chaudhari et al. 2001). Sewage sludge has also been found to be an effective feedstock for biosyngas production with the produced gas' calorific value to be 7000–9500 kJ/m^3 (Domínguez et al. 2008). The basic technology for producing biosyngas is the Fischer–Tropsch process (Fig. 2.9), which can occur in different routes. The thermochemical process can occur at high temperatures (about 1300 °C) or low temperature (about 900 °C) with a catalyst (Chaudhari et al. 2001).

2.4.3 Biohydrogen

Biohydrogen is hydrogen obtained biologically from biomass as an intermediate product from the production of biosyngas. The hydrogen as a component of biosyngas could be isolated through an appropriate purification process and directly used to power hydrogen fuel cells and electric vehicles for electricity production and transport purposes, respectively. Vehicles which are powered by hydrogen are about three times more efficient compared to gasoline powered engines (Jones et al. 2009). Apart from the use of hydrogen as transport fuels and electricity production, it is also used a reactant in hydrogenation and hydrocracking process to produce lower molecular weight compounds. It can also be used for as a good oxygen, sulfur, and nitrogen scavengers. Research and developments are ongoing on how to effectively develop an ecological method that could utilize bacteria to decompose the biomass to produce clean biohydrogen. Biohydrogen has a high energy content of about 33.3 kWh/kg (Demirbas 2004) and emits insignificant amount of environmentally toxic chemicals upon combustion.

Generally, the common technologies used for biohydrogen production from biomass worldwide include novel gasification processes (e.g., direct solar gasification, gasification coupled with water–gas shift process), pyrolysis, supercritical biomass conversion, microbial biomass conversion, biosyngas conversion, etc. After the generation of biosyngas from the Fischer–Tropsch process (Fig. 2.10), biological processes such as biophotolysis, biological water gas shift reaction and fermentation could be employed to separate and upgrade the biohydrogen from the biosyngas. Recent researches have proposed a more efficient method of producing biohydrogen directly from biomass by an integration of novel gasification reactions (HyPr-RING), which integrate the water–hydrocarbon reaction, water–gas shift reaction and absorption of gases in a single reactor under sub and supercritical water conditions (Sato et al. 2003; Lin et al. 2004, 2005). Figure 2.12 also summarizes the process flow of biohydrogen production. The reaction for the HyPr-RING process of biohydrogen production from biomass (carbonaceous material) is shown in Eq. (2.1):

$$C_{(s)} + 2H_2O + CaO \rightarrow CaCO_3 + 2H_2 \qquad (2.1)$$

2.4.4 Biosynthetic Natural Gas (Bio-SNG)

Bio-SNG is a kind of gaseous biofuel produced by the gasification (with methanation) of biomass mostly lignocellulosic materials like oil palm fronds. Bio-SNG has similar chemical compositions as biogas which is generated by the anaerobic digestion of organic wastes. Though bio-SNG production processes are found to be inefficient, bio-SNG can be synthesized from bio-syngas. Noncatalytic gasification at temperatures around 900 °C is reported to effectively produce high levels of methane (Heyne et al. 2010). Zwart et al. (2006) and Tunå (2008) have also

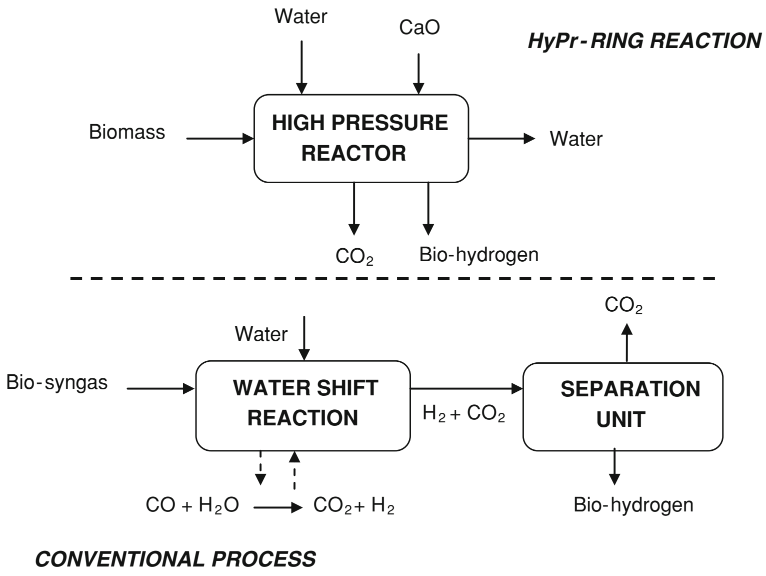

Fig. 2.12 Biohydrogen production from biomass by the HyPr-RING and biological water–gas shift reactions

demonstrated the possibility of generating bio-SNG from biomass in which direct and indirect gasification and methanation at atmospheric pressure were employed. A new technology called G4 bionatural gas process has been developed by the G4 Insights Inc. and Quest Air Technologies Inc. This technology is able to produce quality bio-SNG at high yields from biomass. Though bio-SNG has not gained much attention recently, Sweden (in Güssing) and Austria have initiated a pilot production since 2008 (IEA 2010). In Asian countries like Bangladesh, Armenia, and Pakistan, bio-SNG use in natural gas vehicles has reached a share of about 25 % of their total vehicle fleet (IEA 2010).

2.4.5 Biopropane

Biopropane is a kind of gaseous biofuel which can be synthesized directly from feedstocks like like sugarcane bagasse, switchgrass, biocrude or vegetable oil, biosynthetic gas, glycerol, etc. Presently, in some parts of the USA and EU, biopropane production from lipid feedstocks is supported with federal grants, incentives, and tax programs. Biopropane production technologies include catalytic cracking of acylglycerides, single-reactor technologies, and bioreforming processes. The molecular structure of biopropane is similar to that obtained from petroleum-derived hydrocarbons thus can be blended with conventional propane and use for heating, power generation, and transport applications prior to upgrading.

2.4.6 Global Production and Consumption of Gaseous Biofuels

In Asia and Africa, biogas is produced on small scale for domestic purposes like cooking and residential lighting whilst in the EU, commercial production of biogas from their organic wastes and some types of cereals are available for heating and lighting. In 2009, out of about 230 PJ biogas[15] produced in the EU, only about 10 % was used as vehicle fuel because the cost (about US$ 5–15/GJ biogas) involved in upgrading the gas to avoid engine corrosion was very high (Tilche and Galatoa 2007).

In 2002, the world's total biogas production was estimated at about 92 PJ (with the highest growth rate of about 6 %) with Germany and England contributing the largest amounts (EIA EIA 2011). For instance in 2006, Germany alone had about 850 commercial biogas production plants accounting for about 80 % of the total number of biogas plants in the world by then. The amount of bioelectricity generated from the total biogas produced in the EU in 2006 was about 17,272 GWh of which about 7,338 GWh was contributed by Germany alone (IEA 2010). Biogas used in electrification in Germany contributes about 10 % to the total energy generated from renewable sources. In addition, the EU currently has over 650,000 biogas-powered vehicles running smoothly on their roads as a way of contributing to the move for biofuels sustainability in the near future. Countries like Spain, Sweden, Italy, New Zealand, and Australia also contribute significant share to the world's biogas market. By the end of the year 2020, the world is projected to hit a total of about 779 PJ of biogas production capacity (EIA 2011).

However, the biogas market is still at its infant stage and embodied with a lot of challenges such as high feedstock prices, turmoil in the global credit markets, etc. Supportive government policies in terms of subsidies, incentives, and investments have rather helped boosted the biogas market from collapsing gradually. Presently, the cost of biogas is about € 0.16/kWh. According to the report by Global Industry Analysts Inc., the world's biogas market is forecast to reach about US$ 8.98 billion by 2017. This target would be realized when the urge for reduced dependency on fossil fuels as well as the adoption of efficient methods in production backed by government incentive programs are pursued.

In African countries like Ghana, Tanzania, South Africa, Nigeria, etc., there are millions of biogas plants existing but they operate on only small scale and the biogas from these plants are mostly used for household purposes like cooking. The bigger capacity plants are mainly constructed for hospitals, slaughter houses and big institutions for the purposes of good sanitation. In India, about 1.8 million biogas digesters have been installed since 1990 with their main feedstock being cattle dung. However, by 2005, only about 1.7 million biogas plants were operational (ESMAP 2005). Rural electrification in India is about to be realized with biogas plants under construction with capacity of about 60 kW electricity output (ESMAP 2005). In North America and the USA, there are a few number of biogas plants for medium- and small-scale biogas production. The contribution of commercial production of biogas for electrification to the public grid in these regions has not been realized much due to the low feed-in tariffs (of about EUR 0.05/kWh), which do not make the production profitable (Copel 2009). Though other gaseous biofuels are being used in some parts of the world, their production and consumption capacities are insignificant. Biopropane, for instance, is set to be produced commercially in some parts of Europe and the USA with capacities ranging from 150,000 to 180,000 tons/year (EIA 2011). It would soon be available on the biofuel market as a substitute for LPG and used for transportation purposes.

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[15] This biogas is produced from over 4500 commercial biogas digesters and landfill sites excluding the millions of small scale ones.

2.5 Solid Biofuels for Heat and Power Generation

Biofuels in the form of solids have been in use since man discovered fire for heating. Wood, mostly called firewood, was the first solid biofuel used by the ancient people for cooking and heating until some few decades ago when man discovered alternative ways of utilizing those solid biofuels for cleaner energy production. Currently, most sustainable feedstocks for solid biofuel production are lignocellulosic materials such as forest residues, sawmill wastes, agricultural residues, etc., as they are abundant with limited utilization for value-added bioproducts. In the USA alone, about 95 million dry tons of primary crop residues like corn stovers, wheat straws, rice husks, oat brans, etc., are readily available as wastes for use as solid biofuels. All these wastes could be termed as solid fuels as they can directly be combusted to produce energy for many purposes in all sectors of the economy. This production capacity is projected to double by 2030, which shows a good potential for use as solid biofuels with constant generation. Surprisingly, all other types of biofuels are produced from these solid biofuels. Table 2.4 summarizes the benefits and disadvantages of the three types of biofuels discussed in this chapter. In this section, the main solid biofuels to be discussed are grouped into four namely:

- Woody biomass.
- Herbaceous biomass.
- Fruits and vegetables biomass.
- Blends of two or more of the solid fuels.

Woody biomass is sourced from trees, bushes, and shrubs whilst herbaceous biomass is obtained from plants that are nonwoody and decompose at the end of their growing seasons. Examples include grains, cereals, etc. Fruits and vegetable biomass are obviously obtained from the flesh or seeds of fruits and vegetables such as *Jatropha curcas L.*, oil palm, etc.

In most parts of the world, the most marketed solid biofuels include briquettes, pellets, hog fuel, wood chips, log wood or firewood, biochar, wood shavings,

Table 2.4 Advantages and disadvantages of the types of biofuels

Biofuel type	Advantages	Disadvantages
1. Liquid biofuels	1. Easy to handle 2. Can be transported easily through pipelines 3. Do not leave any residue after combustion 4. Have higher calorific values compared to solid biofuels 5. Produce little or no smoke upon combustion 6. Have relatively low ignition temperature hence burn easily than solid fuels	1. Highly flammable 2. Production technologies and the products are expensive
2. Gaseous biofuels	1. Convenience to use as they don't require any pouring nor priming 2. Can be transported through pipelines 3. Do not leave smoke residues after combustion	1. It produces energy in a less effectively manner at subfreezing temperatures than liquid fuels 2. Highly flammable 3. Difficult to handle 4. Expensive compared to liquid and solid biofuels
3. Solid biofuels	1. Less costly compared to liquid and gaseous biofuels	1. Technology is complex and costly 2. Are environmentally polluting compared to liquid and gaseous biofuels

sawdust, trees bark, straw bales, reed canary grass bales, miscanthus bales, olive residues, energy grains, dried manure, fruit and vegetable seeds, etc. The energy from these fuels is released upon combustion and the combustion conditions may affect the efficiency of the generated energy. Biochar is another important solid biofuel which is produced during pyrolysis.

Briquettes are solid fuels formed from the compression of dried wood chips into small logs or cylinders usually of about 25–70 mm in diameter and 20–25 cm in length (Hosier and Svenningson 1987). Briquetting is usually carried out in order to reduce the bulky nature of the wood chips for easy storage and transportation. Briquettes are normally co-fired together with coal in large power plants for the generation of heat and bioelectricity. Although there are many briquetting plants installed in most parts of the world, they have not been successful due to difficulty in the supply of raw materials and low technological efficiency coupled with high cost of production (Hosier and Svenningson 1987). Briquettes, just like all other solid biofuels normally burn with smoke resulting in environmental degradation thus technological improvement could improve the sustainability of solid biofuels production.

Pellets are solid biofuels with similar properties to briquettes except that pellets are much smaller in dimensions. Pellets are produced firstly by drying the wood chips and grinding then finally extruding under intensive pressure to form the basic shapes. Wood pellet has calorific value of about 18 GJ/ton, which is about half that for fuel oil. Norway is currently among the largest pellets producing countries in the world with a production capacity of about 15,000 tons/year. As at 2010, Russia began producing pellets (with production capacity of about 900,000 tons annually) from the solid residues of their pulp and paper companies, which are used in the generation of heat and electricity. Pellets are also used directly in stoves and furnaces for heat generation in most parts of the world.

In most rural areas of the world, solid biofuels like firewood can directly be burnt in stoves or furnaces to generate heat for cooking and other purposes. Sawdust, woodchips, grass, agricultural residues can also be compacted and directly fired in furnaces and stoves for heating. Tree barks and large agricultural residues are also burnt to produce charcoal, which can be used in stoves to generate energy and use for other various purposes such as the production of reducing agents used in the metallurgical industry. However, more than half of the energy content in these woody materials is lost when they are converted into charcoal. In industrial boilers, solid biofuels such as palm kernel shells, charcoal, etc. can be used to generate clean power. Presently, charcoal production is based on traditional carbonization technology whilst the fast pyrolysis of biomass into charcoal under high pressure is not on commercial scale.

One major problem associated with the combustion of solid biofuels is the considerable amounts of pollutants that they emit. However, the degree of pollution may depend on the type of solid biofuels used. For instance, pellets made from agricultural residues are usually more polluting than wood pellets. Even though solid biofuels emit large amount of dangerous gases, they are better than fossil fuels (see Chaps. 5–7).

2.6 Market Barriers of Biofuels

Compared to fossil fuel, international biofuel trade is nascent. For instance, the international trade of biodiesel and bioethanol among the EU, the USA, and other countries is very small. Basically, the EU consumes its own biodiesel despite the fact that they are the leading producers who must expand their market to the smaller ones. This has been one of the major barriers to the biofuel market growth. Biofuels are currently traded between close neighboring countries and regions of the world and as the biofuel market expands, there would be the need to strengthen possible international trade relationships among countries. Challenges that are faced with the biofuel market originate from the trade with their feedstocks though there exist high international trade relationships between most countries of the world concerning the trade of vegetable oils. For instance, Malaysia and Indonesia have been exporting their palm oil to the EU and the USA to be processed into biodiesel because the EU and the USA have the lead in biofuels technological advancement. The international trade of most oils for biofuels is restricted by tariffs and other migration measures. Imports of biodiesel into the EU are subject to an ‘ad valorem duty’ of about 6.5 % (Doornbosch and Steenblik 2007). Nowadays, large quantities of bioethanol are traded for alcohol beverages, as solvents for industrial applications due to the high cost of bioethanol fuel (without subsidies) on the international market compared to fossil fuels. Brazil still stands as the world’s leading exporter of bioethanol fuel accounting for more than half of the world’s total trade for liquid biofuels. In Africa, though sugarcane is grown in large quantities, bioethanol production is very low due to lack of technology, policies and investments. However, some of the African countries export their sugarcane to other countries to be processed into bioethanol. The major solution to these challenges would be the enaction of standardizations for biofuel production as well as incentives and subsidies for producers. The biofuel market may realize tremendous growth when attractive policy measures are enacted and at the time when fossil fuels finally are exhausted and their prices exceed those of biofuels.

One major barrier to the production and use of biofuels globally is their high cost. For instance, presently, bioethanol production cost is between US$ 0.20 and US$ 0.97/l depending on the feedstock type (Cornland et al. 2001). Bioethanol production from sugarcane (i.e., the sugar) is lower compared to the others with sugar beet bioethanol having the highest production cost. This is due to the high cost of raw materials mostly FGF, which compete with food for land and other resources. Figures 2.13 and 2.14 show the market trends in bioethanol and biodiesel production, respectively.

Technological barriers continue to exist as another challenge to the growth of the biofuel market. Biofuel production processes are energy intensive and consume a lot of fossil fuel during their production hence presenting them costly. Again, process optimization and efficiencies are sometimes complex to achieve especially in the case of bioethanol production from lignocellulose. Also, lack of capital

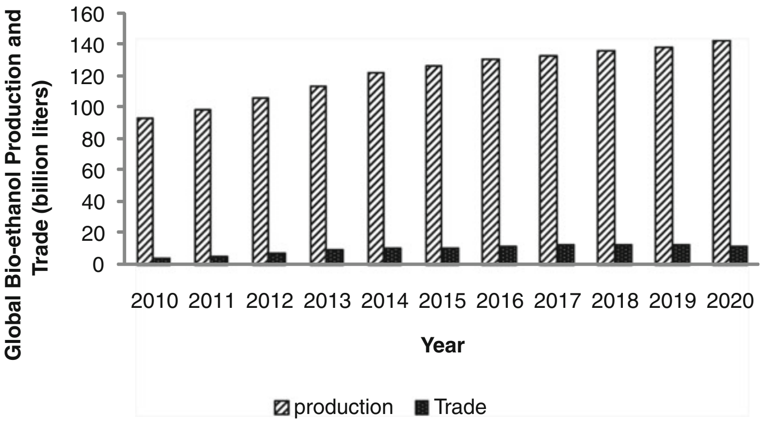

Fig. 2.13 Trend in the global production of bioethanol (OECD-FAO 2011)

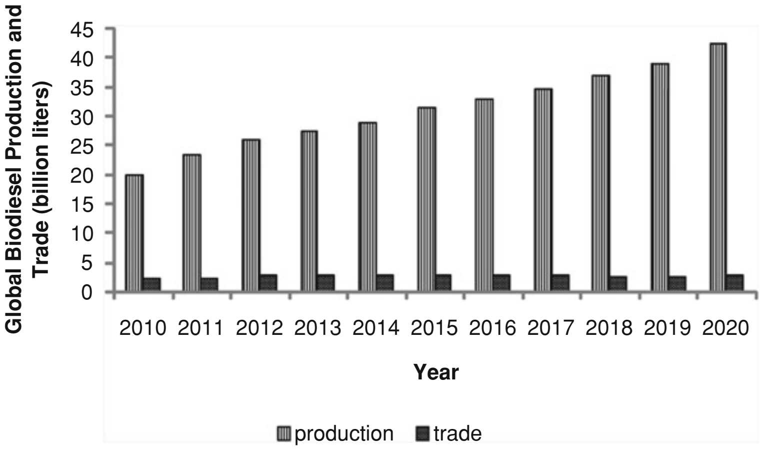

Fig. 2.14 Trend in global biodiesel production and trade (OECD-FAO 2011)

coupled with high transaction costs involved with the production of biofuels have been the contributing factors to the technical barriers to its market growth. Apart from some few biofuels like biodiesel that could be produced on small scale without complex infrastructure, most of the biofuels production could not do without such equipment and infrastructure. For instance, the production of gaseous biofuels especially requires much profound and complex infrastructure to operate successfully and achieve better efficiencies.

Another barrier is in relation with trade. Some types of biofuels do not have specifically laid down sustainability standards and criteria and yet, they are being produced in commercial quantities. This presents the biofuel much more expensive and unattractive compared to fossil fuel presently. For instance, due to lack of laws and regulations on denaturing obligations on bioethanol trade, there exist many trade barriers for its market internationally. The failure of the end users of biofuels to value the products and know the advantages they have over the conventional fuels has been another limitation to the growth of the biofuel market. For instance, the use of some biofuels need engine modification, which create inconveniences to customers hence limiting the market for biofuels. The end users of biofuels mostly lack more knowledge about biofuels and their use.

Another limitation to the growth of biofuel market is attributed to commercialization. FGB are the most abundant type of biofuels under commercialization nowadays. However, with the hope of achieving sustainability, SGB, TGB, and fourth-generation biofuels are encouraged. Yet, commercialization of bioethanol from lignocellulosic materials (which are mainly wastes), for instance, has not been realized much until today though some commercial and pilot productions are ongoing.

2.7 Conclusion

There are many types of biofuels produced and consumed in the world today and these may exist in liquid, solid, and gaseous forms that could be used for various applications. The development of biofuels production technologies is vital for sustainable development because the yield, cost, and environmental impacts may not be encouraging if inappropriate technologies are employed. The production and consumption of biofuels worldwide are recording tremendous growth especially with first-generation biofuels like biodiesel from rapeseed oil. With process improvement in biofuels production technologies, sustainable biofuels development may be realized in the near future.

References

Adebayo GB, Ameen OM, Abass LT (2011) Physico-chemical properties of biodiesel produced from Jatropha Curcas oil and fossil diesel. J Microbiol Biotechnol Res 1:12–16

Akhtar J, Amin NAS (2011) A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. Renew Sust Energy Rev 15:1615–1624

Bacovsky D, Dallos M, Wörgetter M (2010) Status of 2nd generation biofuels demonstration facilities. Report No. T39-P1b, IEA Bioenergy Task 39 Liquid fuels from biomass

Balat M (2005) Current alternative engine fuels. Energy Source 27:569–577

Barsic NJ, Humke AL (1981) Performance and emission characteristic of a naturally aspirated diesel engine with vegetable oil fuels. SAE. 1173-87, paper no. 810262

Bhatti HN, Hanif MA, Faruq U, Sheikh MA (2008) Acid and base catalyzed transesterification of animal fats to biodiesel. Iran J Chem Chem Eng 27:41–48

Bialkowski MT, Pekdemir T, Reuben R, Brautsch M, Towers DP, Elsbett G (2005) Preliminary approach towards a CDI system modification operating on neat rapeseed oil. J KONES 12(1), ISSN 4005 12341 4005

Billaud F, Dominguez V, Broutin P, Busson C (1995) Production of hydrocarbons by pyrolysis of methyl esters from rapeseed oil. JAOCS 72:1179–1154

Boateng AA, Hicks KB, Flores RA, Gutsol A (2006) Pyrolysis of hull-enriched byproducts from the scarification of hulled barley (*Hordeum vulgare L.*). J Anal Appl Pyrolysis 78:95–103

Butler RA (2006) Why is oil palm replacing tropical rainforests? Why are biofuels fueling deforestation? http://news.mongabay.com/, March 2012

CBO (Congressional Budget Office) (2009) Budget and economic outlook. Texas, USA

CDIAC (Carbon Dioxide Information Analysis Center) (2010) The increasing concentration of atmospheric CO_2: how much, when and why? In: Proceedings of 26th session of Erice international seminars on planetary emergencies, Erice, Sicily, Italy, 19–24 Aug 2001

Chaudhari ST, Bej SK, Bakhshi NN, Dalai AK (2001) Steam gasification of biomass-derived char for the production of carbon monoxide-rich synthesis gas. Energy Fuel 15:736–742

Chaudhari ST, Dalai AK, Bakhshi NN (2003) Production of hydrogen and/or syngas ($H_2 + CO$) via steam gasification of biomass-derived chars. Energy Fuel 17:1062–1067

Chaube VD (2004) Benzylation of benzene to diphenylmethane using zeolite catalysts. Catal Commun 5:321–326

Chauvatcharin S, Siripatana C, Seki T, Takagi M, Yoshida T (1998) Metabolisms analysis and on-line physiological state diagnosis of acetone–butanol fermentation. Biotechnol Bioeng 58:561–571

Cigizoglu KB, Ozaklam TK (1997) Use of sunflower oil as an alternative fuel for diesel engines. Energy Source 19:559–566

Coll R, Udas S, Jacoby WA (2001) Conversion of the rosin acid fraction of crude tall oil into fuels and chemicals. Energy Fuel 15:1166–1172

Copel Distribuição SA, Vencedores Da Chamada Pública (2009) List of winners of a tender to sell electricity to the grid in the state of Paraná, Brazil

Cornland D, Johnson FX, Yamba F, Chidumayo EN, Morales M, Kalumiana O, Chidumayo SBM (2001) Sugarcane resources for sustainable development: a case study in Luena, Zambia. Stockholm Environment Institute, Stockholm

Crutzen PJ, Mosier AR, Smith KA, Winiwarter W (2008) N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. Atmos Chem Phys 8:389–395

Cvengroš J, Malík L, Košík M, Šurina I (1985) Fractionation of tall oil. Chem Prum 35:542–545

Davis R, Aden A, Pienkos P (2001) Techno-economic analysis of autotrophic microalgae for fuel production. Appl Energy 88:3524–3531

Demirbas A (2004) Hydrogen rich gas from fruit shells via supercritical water extraction. Int J Hydrog Energy 29:1237–1243

Deshpande AP, Kulkarni K, Kulkarni AD (2011) Supercritical fluid technology in biodiesel production. Chem Mat Res 1:27–32

Diasakou M, Louloudi A, Papayannakos N (1998) Kinetics of the non-catalytic transesterification of soybean oil. Fuel 77:1297–1302

Domínguez A, Fernández Y, Fidalgo B, Pís JJ, Menéndez JA (2008) Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge. Chemosphere 70:397–403

Doornbosch R, Steenblik R (2007) Biofuels: is the cure worse than the disease? Roundtable on sustainable development, OECD (Organization for Economic Co-operation and Development), 11-12 September, Paris, p 57

Dorian JP, Franssen HT, Simbeck DR (2006) Global challenges in energy. Energy Policy 34:1984–1991

Easterly JL (2002) Assessment of bio-oil as a replacement for heating oil. Easterly consulting for Northeast regional biomass program, CONEG Policy Research Center, Inc

EIA (Energy Information Agency of the United States) (2011) International energy statistics. Biofuels production. http://www.eia.gov/cfapps/ipdbproject. Assessed March 2012

ESMAP *(Energy Sector Management Assistance Programme*, World Bank) (2005) Advancing bioenergy for sustainable development—Guideline for Policy-makers and Investors. Report 300/05

Ezeji TC, Qureshi N, Blaschek HP (2003) Production of butanol by *Clostridium beijerinckii* BA101 and in situ recovery by gas stripping. World J Microbiol Biotechnol 19:595–603

Fehrenbacher K (2012) Giga Omni Media (GigaOM), Inc. San Francisco

Flanagan J, Kortegaard K, Pinder DN, Rades T, Singh H (2006) Solubilisation of soybean oil in microemulsions using various surfactants. Food Hydrocoll 20:253–260

Fletcher PDI, Morris JS (1995) Turbidity of oil-in water microemulsion droplets stabilized by nonionic surfactants. Colloid Surf A: Physicochem Eng Aspects 98:147–154

Fond O, Engasser JM, Matta-El-Amouri G, Petitdemange H (1985) The acetone-butanol fermentation on glucose and xylose: regulation and kinetics in batch cultures. Biotechnol Bioeng 28:160–166

Galbe M, Zacchi G (2002) A review of the production of ethanol from softwood. Appl Microbiol Biotechnol 59:618–628

García V, Päkkilä J, Ojamo H, Muurinen E, Keiski RL (2011) Challenges in biobutanol production: how to improve the efficiency? Renew Sust Energy Rev 15:964–980

Goering CE, Schwab AW, Campion RM, Pryde EH (1983) Soyoil-ethanol *microemulsions* as diesel fuel. Trans ASAE 26:1602–1607

Griffith WL, Compere AL, Dorsey GF, West BH (1990) High alcohol microemulsion fuel performance in a diesel engine. SAE paper 902101, Patent (Patent # 5,746,783)

Groot WJ, van der Lans RGJM, Luyben KCAM (1992) Technologies for butanol recovery integrated with fermentations. Process Biochem 27:61–75

Haas MJ (2005) Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. Fuel Process Technol 86:1087–1096

Hebbal OD, Vijaya K, Reddy K, Rajagopal KA (2006) Performance characteristics of a diesel engine with Deccan Hemp oil. Fuel 85:2187–2194

Heyne S, Seemann M, Harvey S (2010) Integration study for alternative methanation technologies for the production of synthetic natural gas from gasified biomass. Chem Eng Trans 21:409–414

Hodge C (2006) Chemistry and emissions of NExBTL. A report prepared for UC Davis, CARB & CEC Meetings on behalf of Neste Oil, California

Honkanen S (2008) Feasibility and market opportunities, a technical report to the World LP Gas Association, Fuels of the Future. Case HVO Renewable Dsl. In: 6th international congress for biofuels of BBE and UFOP, Berlin, 1–2 Dec 2008

Hosier R, Svenningson PJ (1987) Biomass briquettes in the Dominican Republic part I: social and economic feasibility. Biomass 13:199–217

Hunter HF (1996) Method for preparing an alcohol modified vegetable oil diesel fuel. Patent 5380343

IEA (International Energy Agency) (2010) World energy outlook 2010. International Energy Agency Publications, Paris

Joelianingsih MH, Hagiwara S, Nabetani H, Sagara Y, Soerawidjaya TH, Tambunan A, Abdullah K (2008) Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: Kinetic study. Renew Energy 33:1629–1636

Jones SB, Valkenburg C, Walton C, Elliot DC, Holladay JE, Stevens DJ, Kinchin C, Czernik S (2009) Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case. Pacific Northwest National Laboratory, Richland

Joshi RM, Pegg MG (2007) Flow properties of biodiesel fuel blends at low temperatures. Fuel 86:143–151

Jungbluth N, Frischknecht R, FaistEmmenegger M, Steiner R, Tuchschmid M (2007) Life cycle assessment of BTL-fuel production: life cycle impact assessment and interpretation. Deliverables: D5.2.10

Kersten SRA, van Swaaij WP, Lefferts L, Seshan K (2007) In: Centi G, van Santen RA (eds) Catalysis for renewables. Wiley-VCH, Germany

Kim S, Dale B (2002) Allocation procedure in ethanol production system from corn grain: I. system expansion. Int J Life Cycle Assess 7:237–243

Lang X, Dalai AK, Bakhshi NN, Reaney MJ, Hertz PB (2001) Preparation and characterization of bio-diesels from various bio-oils. Bioresour Technol 80:53–63

Lappas AA, Bezergianni S, Vasalos IA (2009) Production of biofuels via coprocessing in conventional refining processes. Catal Today 145:55–62

Larson ED (2008) Biofuel production technologies: status, prospects and implications for trade and development. 2008 United Nations Conference on Trade and Development (UNCTAD)

Levine RB, Pinnarat T, Savage PE (2010) Biodiesel production from wet algal biomass through in situ lipid hydrolysis and supercritical transesterification. Energy Fuel 24:5235–5243

Li L, Du W, Liu D, Wang L, Li Z (2006) Lipase-catalyzed transesterification of rapeseed oils for biodiesel production with a novel organic solvent as the reaction medium. J Mol Catal B Enzym 43:58–62

Lif A, Holmberg K (2006) Water-in-diesel emulsions and related systems. Adv Colloid Interface Sci 123–126:321–329

Lim S, Teong LK (2010) Recent trends, opportunities and challenges of biodiesel in malaysia: an overview. Renew Sust Energ Rev 14:938–954

Lin SY, Harada M, Suzuki Y, Hatano H (2004) Continuous experiment regarding hydrogen production by coal/CaO reaction with steam (I) gas products. Fuel 83:869–874

Lin SY, Harada M, Suzuki Y, Hatano H (2005) Process analysis for hydrogen production by reaction integrated novel gasification (HyPr-RING). Energy Conv Manage 46:869–880

Liu Y, Lotero E, Goodwin JG, Mo X (2007) Transesterification of poultry fat with methanol using Mg-A1 hydrotalcite derived catalysts. Appl Catal A 331:138–148

Lü J, Sheahan C, Fu P (2011) Metabolic engineering of algae for fourth generation biofuels production. Energy Environ Sci 4:2451–2466

Machacon HTC, Seiichi S, Takao K, Hisao N (2001) Performance and emission characteristics of a diesel engine fueled with coconut oil—diesel fuel blend. Biomas Bioenergy 20:63–69

Mansur MC, O'Donnell MK, Rehmann MS, Zohaib M (2010) ABE fermentation of sugar in Brazil. Senior Design Reports (CBE), Department of Chemical & Biomolecular Engineering, University of Pennsylvania

Marchetti JM, Miguel VU, Errazu AF (2008) Techno-economic study of different alternatives for biodiesel production. Fuel Process Technol 89:740–748

Marland G (2010) Accounting for carbon dioxide emissions from bioenergy systems. J Ind Ecol 14:866–869

Martin M, Prithviraj D (2011) Performance of preheated cotton seed oil and diesel fuel blends in a compression ignition engine. Jordan J Mechan Ind Eng 5:235–240

Maschio G, Lucchesi A, Stoppato G (1994) Production of syngas from biomass. Bioresour Technol 48:119–126

Mittelbach M, Gangl S (2001) Long storage stability of biodiesel made from rapeseed and used frying oil. J Am Oil Chem Soc 78:573–577

Moser BR (2009) Biodiesel production, properties and feedstocks. In Vitro Cell Dev Biol-Plant 45:229–266

MPOB (Malaysian Palm Oil Board) (2010) Overview of the Malaysia palm oil industry. www.mpob.gov.my, Accessed 20 June 2011

Murayama T (1984) Low carbon flower build -up, low smoke and efficient diesel operation with vegetable oil by conversion into monoesters and blending with diesel or alcohol. SAE 5:292–301

Nasikin M, Susanto BH, Hirsaman MA, Wijanarko A (2009) Biogasoline from palm oil by simultaneous cracking and hydrogenation reaction over Nimo/zeolite catalyst. World Appl Sci 5:74–79

Neumann GT, Hicks JC (2012) Novel Hierarchical cerium-incorporated MFI zeolite catalysts for the catalytic fast pyrolysis of lignocellulosic biomass. ACS Catal 2:642–646

Nguyen T, Do L, Sabatini DA (2010) Biodiesel production via peanut oil extraction using diesel-based reverse-micellar microemulsions. Fuel 89:2285–2291

Niehaus RA, Goering CE, Savage LD, Sorenson SC (1985) Cracked soybean oil as a fuel for diesel engine. ASAE Paper no. 85-1560

OECD-FAO (Organization for Economic Cooperation and Development-Food and Agriculture Organization) (2011) OECD-FAO agricultural outlook 2011–2020

Ofori-Boateng C, Kwofie EM (2009) Water scrubbing: a better option for *biogas* purification for effective storage. World Appl Sci 5:122–125

Ofori-Boateng C, Lee KT (2011) Feasibility of jatropha oil for biodiesel: economic analysis. In: Proceedings of the world's renewable energy congress, Linkoping, Sweden, 9-13th May, 2011. Available at http://dx.doi.org/10.3384/ecp11057463. Accessed on 28th July, 2012

Panigrahi S, Dalai AK, Chaudhari ST, Bakhshi NN (2003) Synthesis gas production from steam gasification of biomass-derived oil. Energy Fuel 17:637–642

Phillips JA, Humphrey AE (1983) An overview of process technology for the production of liquid fuels and chemical feedstocks via fermentation. In: Wise DL (eds) Organic chemicals from biomass, The Benjamin/Cummings Publishing Co, Inc, Menlo Park, California pp 249–304

Pramanik K (2003) Properties and use of Jatropha Curcas oil and diesel fuel blends in compression ignition engine. Renew Energy 28:239–248

Prasad CHSN (2010) Experimental investigation on performance and emission characteristics of diesel engine using bio-diesel as an alternate fuel. Ph.D Thesis, Faculty of Mechanical Engineering, JNTUH College of Engineering, Hyderabad

Qureshi N, Meagher MM, Huang J, Hutkins RW (2002) Acetone butanol ethanol (ABE) recovery by pervaporation using silicalite-silicone composite membrane from fed-batch reactor of *Clostridium acetobutylicum*. J Membr Sci 187:93–102

Radich A (2004) Biodiesel performance, cost and use, energy information administration. United States Department of Energy, Washington

Ramey D, Yang S (2004) Production of butyric acid and butanol from biomass. Final report, US Department of Energy, Ohio

Rao ND, Premkumar BS, Yohan M (2012) Performance and emission characteristics of straight vegetable oil-ethanol emulsion in a compression ignition engine. ARPN J Eng Appl Sci 7:1819–6608

Reaney M (1997) Agriculture and agri-food Canada, Saskatoon, Saskatchewan, Personel Communications

REN21 (Renewable Energy Policy Network for the 21st century) (2010) Renewables 2010, Global status report, REN21 Secretariat, Paris, France

RFA (Renewable Fuels Association) (2010) Ethanol facts: trade. http://www.ethanolrfa.org/pages/ethanolfacts-trade

Richards B, Herndon FG, Jewell WJ, Cummings RJ, White TE (1994) In situ methane enrichment in methanogenic energy crop digesters. Biomass Bioenergy 6:274–275

Rosca R, Zugravel M (1997) The use of sunflower oil in diesel engines. SAE Paper no. 972979

Sadaka S, Boateng AA (2009) Pyrolysis and Bio-oil. University of Arkansas publication - FSA1052, Fayetteville, Arkansas, United States. Available at http://www.uaex.edu/Other_Areas/publications/PDF/FSA-1052.pdf. Accessed on 11th January, 2011

Saka S, Kusdiana D (2001) Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel 80:225–231

Sapvan SM, Nasjuki HH, Azlan A (1996) Use of palm oil as diesel fuel substitute. J Power Energy 210:47–53

Sato S, Lin SY, Suzuki Y, Hatano H (2003) Hydrogen production from heavy oil in the presence of calcium hydroxide. Fuel 82:561–567

Schlick ML, Hanna MA, Schnstock JL (1988) Soybean and sunflower oil performance in a diesel engine. Trans ASAE 31:1345–1349

Schwab AW, Bagby MO (1987) Freedman B. Preparation and properties of diesel fuels from vegetable oils. Fuel 66:1372–1378

Shapouri H, DuIeld JA, Wang M (2002) The energy balance of corn ethanol: an update. Agricultural economic report 813. US Department of Agriculture, Washington

Shimada Y, Watanabe Y, Sugihara A, Tominaga Y (2002) Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing. J Mol Catal B Enzym 17:133–142

Shrestha D, Gerpen JV (2010) Biodiesel from oilseed crops, In: Singh BP (ed) Industrial crops and uses. CABI, Wallingford, pp 512, 140–156. ISBN-13 9781845936167

Solantausta Y, Nylund N, Gust S (1994) Use of pyrolysed oil in a test diesel engine to study the feasibility of a diesel power plant concept. Biomass Bioenergy 7:297–306

Solantuasta Y (2006) Co-processing of upgraded bio-liquids in standard refinery units-BIOCOUP. In: Proceedings of the european conference on biorefinery research, 19th to 20th Oct Helsinki, Finland. Available at http://ec.europa.eu/research/energy/gp/gp_events/biorefinery/article_3764_en.htm. Accessed on 10th August, 2012

Song YC, Kwon SJ, Woo JH (2004) Mesophilic and thermophilic temperature co-phase anaerobic digestion compared with single-stage mesophilic- and thermophilic digestion of sewage sludge. Water Res 38:1653–1662

Srivastava A, Prasad R (2000) Triglycerides-based diesel fuels. Renew Sust Energy Rev 4:111–133

Tadashi Y (1984) Low carbon build up, low smoke and efficient diesel operation with vegetable oil by conversion to monoesters and blending of diesel or alcohols. SAE 841161

Tamunaidu P, Bhatia S (2007) Catalytic cracking of palm oil for the production of biofuels: optimization studies. Bioresour Technol 98:3593–3601

Tilche A, Galatoa M (2007) The potential of anerobic digestion for reducing GHG emissions. In: 11th world congress on anearobic digestion, Brisbane, 23–27 Sept 2007

Trostle C (2008) BioEnergy and the Texas South Plains. Associate Professor & Texas AgriLife Extension Service Agronomist, Texas A&M System—Lubbock. http://lubbock.tamu.edu/whatsnew/bioenergyjan08.pdf. Accessed Dec 2011

Tunå P (2008) Substitute natural gas from biomass gasification. Synopsis of Master Thesis, Department of Chemical Engineering, Lund University, Sweden

Vellguth G (1983) Performance of vegetable oil and their monoesters as fuels for diesel engines. SAE 831358

Wang YD, AZ-Shemmeri T, Eames P, McMullan J, Hewitt N, Huang Y (2006) An experimental investigation of the performance and gaseous exhaust emission of a diesel engine using blends of a vegetable oil. Appl Therm Eng 26:1684–1691

Webber ME, Amanda DC (2008) Cow power. In: The news: short news items of interest to the scientific community. Science and children os 46.1:13. Gale, United States

Williams PT, Chishti HM (2000) Two stage pyrolysis of oil shale using a zeolite catalyst. J Anal Appl Pyrolysis 55:217–234

WWI (Worldwatch Institute) (2006) Biofuels for transport: global potential and implications for energy and agriculture. Report prepared by Worldwatch Institute for the German Ministry of Food, Agriculture and Consumer Protection (BMELV) in coordination with the german agency for technical cooperation (GTZ) and german agency of renewable resources (FNR), Earthscan, London

Yoon SH, Park SH, Lee CK (2008) Experimental investigation on the fuel properties of biodiesel and its blends at various temperatures. Energy Fuel 22:652–656

Zhu B, Gikas P, Zhang R, Lord J, Jenkins B, Li X (2009) Characteristics and biogas production potential of municipal solid wastes pretreated with a rotary drum reactor. Bioresour Technol 100:1122–1129

Zwart R, Boerrigter H, Van der Drift A (2006) The impact of biomass pretreatment on the feasibility of overseas biomass conversion to Fischer-Tropsch products. Energy fuel 20:2192–2197